

# IONS, ELECTRONS, AND IONIZING RADIATIONS

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## PREFACE TO FIRST EDITION

IN bringing forward yet another book on the subject which, for want of a brief comprehensive title, I have been compelled to describe as Ions, Electrons, and Ionizing Radiations it seems desirable to indicate briefly the purpose it is intended to fulfil. It is not a popular exposition of the "new Physics," nor is it a compendious synopsis of the whole subject. The subject is in fact now so extensive that it is doubtful if such a treatise could be produced in less than half a dozen volumes. The present volume is intended solely as a text-book from which students who have been grounded in the more elementary portions of Physics might obtain a systematic knowledge of its latest developments. The subject has now reached such dimensions that a student entering upon it for the first time needs the same help and guidance which is already provided for him in other branches of Physics by numerous text-books, elementary and advanced. This need I have attempted to supply.

In doing so I have found myself compelled to exercise the liberties which the writer of any text-book must take with his material, if his purpose in writing is to be fulfilled. I have selected freely from the great mass of experimental researches and theories the most fundamental, most important, and best established, and have arranged them in the order which seemed most straightforward and easy for the student. The great classical experiments in the subject I have endeavoured to describe in some detail, exactly as they were first performed,

even when their method has been improved upon by later experimenters. Experiments such as those of Sir J. J. Thomson on the cathode rays, and Kaufmann on the variation of mass with velocity, like Faraday's experiments on electromagnetic induction of currents and Joule's determination of the Mechanical Equivalent of Heat, are landmarks in the history of progress and should be preserved as far as possible intact. In the case of many less epoch-making experiments I have felt at liberty to omit or to modify unimportant details where such changes seemed necessary to make the principles involved clearer to the student.

In the same way I have simplified the mathematical treatment of the subject wherever possible, not merely in the interests of students whose mathematical equipment is not very extensive, but also because I have found in practice that even in the case of students who are better equipped a real understanding of the argument and of the physical principles involved in it is more readily attained if the mathematical analysis is not too complicated. The ability to reproduce several pages of mathematical symbols is no measure of, and certainly no adequate substitute for, a real understanding of the nature of the argument.

Within its limits it is hoped that the present volume furnishes a reasonably complete account of the present state of the subject, that nothing of real importance has been omitted, nor too many unimportant details included, to the confusion of the clear outlines of the subject.

In a book which from its nature lays no claim to originality, no detailed list of acknowledgements is required. I have consulted freely all the books and memoirs given in the list of references at the end of this volume, together with numerous original papers and memoirs on the subject. I am, perhaps, even more indebted to that fund of information and ideas,



## PREFACE

which is acquired almost unconsciously by one who has had the privilege of working in the Cavendish Laboratory under Professor Sir J. J. Thomson, and of enjoying there the conversation of many of those whose researches have made the present volume possible. I should also like to express my best thanks to Mr C. T. R. Wilson for allowing me to reproduce the photographs of tracks of ionizing particles which form figures 16, 17 and 18, and to Mr E. V. Appleton for his kindness in reading the proofs.

J. A. C.

CAMBRIDGE,  
*August, 1919*

## PREFACE TO FOURTH EDITION

It is, perhaps, a moot point whether the recent additions to our knowledge of the subject matter of this volume have been greater on the experimental or on the theoretical side. Taken together they constitute a mass of material which, while it emphasises the need for a text-book alluded to in the preface to the first edition, makes the task of providing such a book one of increasing difficulty. The publishers have very kindly allowed me a perfectly free hand in the preparation of this fourth edition, and I have availed myself very freely of the opportunity thus afforded.

The chapter on X-rays, and that on the Electron Theory of Matter, have been practically rewritten, and much enlarged, and extensive additions and alterations, illustrated by new diagrams, have been made to most of the other chapters. I should like here to express my thanks to Dr G. Shearer for the X-ray spectrogram (Fig. 45) and to Dr Aston and the Publishers for permission to reproduce the Mass spectrogram (Fig. 46). New

sections have been added dealing with ionization and resonance potentials, with Langmuir's theory of thermo-electric emission, with the collision of  $\alpha$ -particles with atoms and the structure of the nucleus, with Ellis's important investigations into the  $\gamma$ -ray spectrum, and with the emission of electrons both by light and by X-rays. Parts of the subject which have come into greater prominence since the book was first written have received fuller treatment, while sections dealing with subjects which now appear to be of less vital importance have occasionally been compressed, or eliminated. Emphasis has been laid throughout on the quantum hypothesis, and in particular on its experimental basis, and a far fuller account than was possible in the earlier editions has been given of its applications to the theory of atomic structure. These extensive changes have necessitated the re-numbering of the paragraphs and figures practically throughout the book.

References have been added to the various chapters, but these lay no claim to completeness. Where choice was possible, I have selected the papers most likely to be readily available to English-speaking students. Full bibliographies are usually to be found in the works quoted under the heading General References.

While it would perhaps be too much to expect that the author's selection of material from so vast a store will meet with universal approval in every detail, it is hoped that the volume, in its new edition, reflects faithfully once more the standpoint of modern physics, and that it will prove itself a useful guide and companion to students commencing the study of this most fascinating and vigorous branch of science.

J. A. C.

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READING.  
*September, 1924*

# CONTENTS

## CHAPTER I

### INTRODUCTION

ART	PAGE
1. Electrons . . . . .	1
2. Conduction through gases . . . . .	3
3. Radio-active substances and their radiations . . . . .	4

## CHAPTER II

### THE PASSAGE OF A CURRENT THROUGH AN IONIZED GAS

4	Conductivity of gases in the normal state . . . . .	7
5	Ionization theory of gaseous conduction . . . . .	9
6	Methods of measuring the current through a gas . . . . .	10
7.	Measuring instruments . . . . .	11
8.	The ionization chamber . . . . .	14
9	Variation of the current with the potential across the gas . . . . .	15
10.	Variation of the saturation current with the distance between the electrodes, and the pressure of the gas . . . . .	17
11.	Theory of conduction through gases . . . . .	17
12.	Motion of the ions under a uniform electric field . . . . .	19
13	Theoretical relation between current and potential . . . . .	20

## CHAPTER III

### THE PROPERTIES OF THE GASEOUS IONS

14.	Measurement of ionic mobilities Rutherford's method, Langevin's method . . . . .	23
15	Mobilities of the ions in different gases . . . . .	27
16.	Approximate calculation of the mobility of an ion . . . . .	28
17.	Effect of pressure on the mobility of the ions . . . . .	30
18.	Measurement of the coefficient of recombination . . . . .	32

## CHAPTER IV

## THE CHARGE ON AN ION

ART.		PAGE
19	Condensation of water drops on ions . . . .	36
20	C. T. R. Wilson's cloud experiments . . . .	37
21.	C. T. R. Wilson's later condensation experiments . . . .	41
22.	Application to the determination of $e$ . Thomson's method. Balancing method . . . . .	41
23	Millikan's experimental determination of $e$ . . . .	43
24	Perrin's determination of $e$ from the Brownian movement . . . .	46
25	Summary of results . . . . .	50

## CHAPTER V

IONIZATION BY COLLISION—THE  
SPARK DISCHARGE

26	Ionization currents with large voltages . . . . .	52
27	Difference in the effects produced by positive and negative ions . . . .	54
28	Expression for the current through the gas when ionization by collision occurs . . . . .	56
29.	Townsend's experiments . . . . .	57
30.	Variation of $\alpha$ with pressure and field . . . . .	60
31	Minimum velocity required to produce ionization . . . . .	62
32	Resonance Potentials . . . . .	63
33	Ionization by collisions with the positive ions . . . . .	65
34.	The spark discharge . . . . .	67
35	Sparkling potential for parallel plate electrodes . . . . .	69
36	Paschen's law . . . . .	70
37.	Variation of sparking potential with temperature . . . . .	71
38	The brush discharge . . . . .	72
39	The dark discharge . . . . .	73

## CHAPTER VI

## THE PHENOMENA OF THE DISCHARGE TUBE

40.	Phenomena of the discharge in a gas at low pressure . . . .	75
41.	Investigation of the intensity of the field in various parts of the discharge . . . . .	77
42	Number of ions in various parts of the discharge . . . . .	79
43	The cathode fall of potential . . . . .	81
44.	Theory of the discharge . . . . .	82

## CHAPTER VII

## CATHODE RAYS AND POSITIVE RAYS

ART	PAGE
45 Cathode rays . . . . .	86
46 Motion of a charged particle under the action of a magnetic field . . . . .	90
47 Motion of a charged particle under the joint action of electric and magnetic forces . . . . .	92
48 Thomson's method of determining $e/m$ and $v$ for cathode rays . . . . .	95
49 Kaufmann's method of determining $e/m$ . . . . .	98
50 The magnetic spectrum . . . . .	98
51 Numerical value of $e/m$ . . . . .	99
52 Direct measurement of the velocity of cathode rays . . . . .	100
53 The positive rays . . . . .	101
54 Thomson's experiments on the positive rays . . . . .	102
55 Positive ray parabolas . . . . .	105
56 Negative parabolas . . . . .	109
57 Positive ray analysis . . . . .	110
58 The mass-spectrograph Aston's experiments . . . . .	111
59 Electrical method of measuring positive rays . . . . .	114
60 Secondary effects . . . . .	115

## CHAPTER VIII

## EMISSION OF ELECTRICITY BY HOT BODIES

61 Loss of charge from a hot body . . . . .	117
62 Nature of the negative thermions . . . . .	118
63 Variation of the current with temperature . . . . .	119
64 Theory of thermionic emission . . . . .	119
65 Evidence for the theory of thermionic emission . . . . .	122
66 Discharge of negative electricity by various substances . . . . .	123
67 Discharge of positive electricity . . . . .	126
68 The current through a thermionic valve Langmuir's Law . . . . .	127
69 Conductivity of flames . . . . .	130
70 Distribution of potential between two electrodes in a flame . . . . .	131
71 Conductivity of salt vapours . . . . .	131
72 Maximum current carried by salt vapours . . . . .	135

## CHAPTER IX

## PHOTO-ELECTRICITY

73 The photo-electric effect . . . . .	137
74 Ionization of gases by ultra-violet light . . . . .	138
75 Velocity of emission of the photo-electrons . . . . .	140
76 The quantum theory . . . . .	142

ART	PAGE
77. Distribution of velocities among the photo-electrons . . . . .	145
78. Magnitude of the photo-electric effect . . . . .	145
79. Variation of the photo-electric effect with wave length and state of polarization . . . . .	148
80. Photo-electric fatigue . . . . .	150
81. Photo-electric effect in non-metals . . . . .	150
82. Phosphorescence and the photo-electric effect . . . . .	151

## CHAPTER X

## X-RAYS

83. Production of X-rays . . . . .	153
84. Radiation emitted by the stoppage of a moving electrified particle Classical Theory . . . . .	156
85. The scattering of X-rays by matter . . . . .	160
86. Polarization of the scattered radiation . . . . .	161
87. Energy of the scattered radiation . . . . .	163
88. Interference phenomena with X-rays . . . . .	165
89. Theory of Laue's experiments on the diffraction of X-rays by crystals . . . . .	166
90. Reflection of X-rays by crystal planes Experiments of Bragg . . . . .	169
91. The X-ray spectrometer . . . . .	173
92. Determination of the wave length of X-rays . . . . .	175
93. The X-ray spectra Continuous background . . . . .	178
94. The X-ray spectra The characteristic radiations . . . . .	180
95. The absorption of X-rays . . . . .	183
96. Characteristic secondary radiation . . . . .	186
97. Conditions for the direct excitation of characteristic radiation . . . . .	189
98. The theory of X-ray spectra . . . . .	192
99. Secondary corpuscular radiation . . . . .	194
100. Ionization by X-rays . . . . .	199

## CHAPTER XI

THE  $\alpha$ -RAYS

101. Properties and nature of the $\alpha$ -rays . . . . .	202
102. Nature of the $\alpha$ -particle . . . . .	203
103. Determination of the charge on an $\alpha$ -particle . . . . .	203
104. Passage of the $\alpha$ -rays through matter . . . . .	206
105. Bragg's experiments on the range of the $\alpha$ -particles . . . . .	209
106. The stopping power of an atom for $\alpha$ -particles . . . . .	213
107. The scattering of the $\alpha$ -particles . . . . .	214
108. The collision of $\alpha$ -particles with atoms . . . . .	219

## CHAPTER XII

THE  $\beta$ - AND  $\gamma$ -RADIATIONS

ART		PAGE
109	Nature of the $\beta$ -rays . . . . .	222
110.	Determination of $e/m$ and $v$ for the $\beta$ -rays . . . . .	223
111.	Electromagnetic mass . . . . .	225
112	Variation of the mass of an electron with velocity . . . . .	227
	experiments . . . . .	227
113	Passage of the $\beta$ -rays through matter . . . . .	229
114	The scattering of the $\beta$ -rays . . . . .	231
115	Nature and properties of the $\gamma$ -rays . . . . .	233
116	Absorption of $\gamma$ -rays . . . . .	234
117	Characteristic $\gamma$ -radiations . . . . .	234
118	Determination of the wave length of $\gamma$ -rays . . . . .	235
119	Secondary $\gamma$ -rays . . . . .	237
120	Production of $\gamma$ -rays from $\beta$ -rays . . . . .	237
121	Characteristic $\beta$ -rays . . . . .	240
122	Origin of characteristic $\gamma$ -radiation . . . . .	241

## CHAPTER XIII

## RADIO-ACTIVE CHANGES

123	Disintegration of uranium . . . . .	243
124	Theory of radio-active change . . . . .	246
125	Theory of successive transformations . . . . .	248
126	Radio-active equilibrium . . . . .	251

## CHAPTER XIV

## RADIUM AND ITS PRODUCTS

127	The nature and properties of radium . . . . .	256
128	Radium emanation . . . . .	257
129	Elementary nature of radium emanation . . . . .	258
130.	Rate of decay of radium emanation . . . . .	259
131	Rate of escape of the emanation . . . . .	261
132	Measurement of the volume of the emanation in equilibrium with one gram of radium . . . . .	261
133.	The active deposit from radium emanation . . . . .	262
134	Recoil atoms . . . . .	264
135.	Analysis of the active deposit of rapid change . . . . .	265
136.	Separation of the products by the method of "recoil" . . . . .	269
	Complex nature of radium C . . . . .	269
137	The radio-active product of slow change . . . . .	271
138	The radio-activity of thorium and actinium . . . . .	272
	Tables of radio-active series . . . . .	272
139	Position of the radio-active elements in the Periodic Table . . . . .	275

## CHAPTER XV

## SOME PROBLEMS IN RADIO-ACTIVITY

ART.	PAGE
140. Uranium and the origin of radium . . . . .	278
141. Production of helium from uranium. Geological age . . . . .	279
142. The end-product of the uranium chain . . . . .	280
143. The heating effect of radium . . . . .	281
144. The range of the $\alpha$ -particles and the period of decay . . . . .	284
145. Radio-activity of ordinary matter . . . . .	285

## CHAPTER XVI

## THE ELECTRON THEORY OF MATTER

146. The constitution of the atom . . . . .	287
147. Constitution of atomic nuclei . . . . .	289
148. Arrangement of electrons in an atom. The Thomson Atom . . . . .	292
149. The Rutherford-Bohr atom . . . . .	295
150. Bohr's theory of the hydrogen spectrum . . . . .	296
151. The normal hydrogen atom . . . . .	300
152. Elliptic orbits. Sommerfeld's theory . . . . .	301
153. The electronic structure of the atom . . . . .	303
154. Electron grouping and the periodic classification of the elements . . . . .	305
155. Electron theory of valency, and chemical combination . . . . .	307
156. The theory of X-ray spectra . . . . .	309
157. Orientation of the atom. The "third" quantum number . . . . .	311
158. Emission of light. The Zeeman effect . . . . .	312
159. Electron theory of metallic conduction . . . . .	316
160. Relation of electrical and thermal conductivities. Law of Wiedemann and Franz . . . . .	318
161. Thermoelectric effects . . . . .	321
TABLE OF ATOMIC DATA . . . . .	323
INDEX . . . . .	324

## PLATES

## PLATE

I	Figs. 16, 17, 18 . . . . .	TO FACE PAGE 41
II	Figs. 44, 45, 46 . . . . .	" " 110



## CHAPTER I

### INTRODUCTION

**1 Electrons** The phenomena which form the subject of the present text-book have been, in the main, brought to light within the last thirty years, and represent a mass of research which in its volume and its rapidity of growth is unprecedented in the annals of physical science. Progress has been made upon three main lines, but these are so intermingled, and break in upon each other and support each other at so many points that it is impossible to deal with one without assuming at least a casual acquaintance with the main results of the others. Owing partly to the newness of the subject, but mainly to its magnitude the accounts given of the subject in text-books on general electricity are usually somewhat inadequate, and such knowledge cannot be postulated in a student of physics who approaches the subject as a whole for the first time. It will be desirable therefore before commencing a detailed study of the phenomena to state broadly the results and conclusions at which we hope to arrive.

Historically the subject may be said to have taken its origin in experiments on the discharge of electricity through gases at low pressure contained in some form of discharge tube. When a high tension discharge is sent through a gas at low pressure (say some fraction of a millimetre of mercury) the gas becomes luminous shewing a series of glows and striae (see Fig. 31), which are often very beautiful, but which, at the time of their discovery, were very difficult to explain on the current theories of the time. If the pressure is sufficiently low, a series of streamers known as the cathode rays can be observed proceeding in straight lines from the cathode and crossing the other glows in the tube. The experiments of Sir William Crookes led him to the conclusion that these rays were material

was placed beyond all reasonable doubt by the experiments of C. T. R. Wilson, who shewed that these ions could serve as nuclei for the condensation of drops of water in a supersaturated space. The ions were thus rendered visible by the deposition of the water upon them, and could readily be observed, and even photographed. Photographs such as that of Fig. 17, which represents the track of a cathode particle through air, make it certain that the production of conductivity in a gas by these ionizing radiations is due to the formation in the gas of definite charged systems.

3 **Radio-active substances and their radiations.** The discovery of X-rays and the somewhat startling manner in which these rays were able to penetrate considerable thicknesses of materials which were opaque to ordinary light naturally led to an exhaustive search among natural substances to see if any of these emitted radiations having properties at all resembling those of X-rays. The research was pursued with vigour by Becquerel and afterwards by the Curies, and led to the discovery that radiations possessing the properties of penetrating opaque substances and of causing conductivity in gases were emitted by the salts of uranium and thorium. The subsequent observation that naturally occurring ores of uranium were several times more active than the metal itself led to the isolation of radium, and subsequently of other similar substances which were found to possess these properties in a very remarkable degree. Substances which are capable of emitting spontaneously these ionizing radiations are classed together under the title *radio-active substances*.

It has been shewn that each radio-active substance is a definite chemical element, and that its activity is due to a spontaneous decomposition or disintegration as it is usually termed of the radio-active atom into one of smaller weight, the process taking place according to definite laws which have been determined. This naturally leads us to the view that the atoms of the various chemical elements are not essentially different in kind but represent complex systems built up out of one or two elementary forms according to certain definite laws.

On further investigation it was found that the rays given out by these radio-active substances were of three kinds, which were denoted by the non-committal symbols  $\alpha$ ,  $\beta$ , and  $\gamma$ . This nomenclature is convenient and has been retained. All three types possess in common with X-rays the properties of converting a gas into a conductor, of affecting a photographic plate, and of causing luminescence in a fluorescent screen. In other respects however they differ very markedly in their properties.

The  $\alpha$ -rays were found to be positively charged and were of the size of atoms. They have recently been proved to consist of helium atoms which have lost two electrons and thus possess a positive charge of  $2 \times (4.77 \times 10^{-10})$  or  $9.5 \times 10^{-10}$  c.s.u. They are very easily absorbed in matter being completely stopped by 1/10th mm of aluminium or a few centimetres of air at atmospheric pressure. They produce very intense ionization in the gas through which they pass. Their velocity depends on the substance from which they are ejected, their nature is always the same.

The  $\beta$ -rays on the other hand carry a negative charge. They can penetrate much greater thicknesses of matter than the  $\alpha$ -rays, producing measurable effects through a thickness of even a centimetre of aluminium. The ionization they produce in a gas is however small compared with that of the  $\alpha$ -rays. Their nature is found to be identical with that of the cathode rays. They consist of electrons, carrying the universal electronic charge, and differ from the cathode rays only in velocity. Whereas it is difficult to obtain cathode rays with a velocity much greater than one-tenth that of light, the  $\beta$ -rays from radium possess velocities which range up to within one or two per cent of that of light itself.

The  $\gamma$ -rays are exceedingly penetrating, those from radium producing quite measurable effects through a thickness of 20 or 30 cms of iron. Their ionizing power is small, as the fraction of their energy which can be absorbed by any reasonable thickness of gas is minute. They are now known to be pulses in the ether of very short wave length (about  $10^{-8}$  cm). X-rays are also ether pulses but of a considerably longer wave length,

generally about  $10^{-8}$  cm. The  $\gamma$ -rays and the X-rays thus represent the extreme end of the electromagnetic wave scale, in other words, they are ultra-violet rays of extremely short wave length. Between the radiations usually denoted as ultra-violet and X-rays there is however a wide gulf, the shortest ultra-violet rays at present known having a wave length of rather more than  $10^{-5}$  cms. Radiations of intermediate wave length have been produced in high vacua, but practically nothing is known of their properties. In spite of this wide gap we shall see that these ultra-violet rays have many properties in common with X-rays, including the property of producing conductivity in a gas.

## CHAPTER II

### PASSAGE OF A CURRENT THROUGH AN IONIZED GAS

**4 Conductivity of gases in the normal state** A gas in its normal state is one of the best insulators of electricity known. It was indeed for a long time a moot point whether gases conducted electricity at all, and whether the gradual loss of charge which always occurs with charged bodies might not be due to slight defects in the insulating qualities of the solid materials used to support

the body. The matter was settled by C. T. R. Wilson using the ingenious apparatus shewn in Fig. 1. The gas is enclosed in a large spherical vessel which is silvered inside to make it conducting. The charged system takes the form of a brass rod carrying a pair of thin gold leaves. In this way the charged body is made to serve as its own electroscope. Since the electrical capacity of a system such as this is very small,

a very small loss of charge will be sufficient to produce a large fall of potential, and hence a considerable movement of the gold leaves, which were closely observed with a long focus microscope having a micrometer scale in the eye piece. The apparatus was thus exceedingly sensitive.

The end of the rod carrying the gold leaves was fused into a block of sulphur *S*, sulphur when carefully prepared being an exceedingly good insulator. The sulphur block was supported

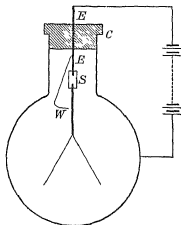


FIG. 1

by another brass rod  $E$  passing through an ebonite cork in the neck of the vessel

The rod  $E$  is charged to some suitable potential (about 400 volts) and is maintained at this potential throughout the experiment, most conveniently by connecting it to one end of a cabinet of small accumulator cells, the other terminal of which is connected to the silver coating of the vessel. Contact between  $E$  and the gold leaves can be made, when required, by means of the fine iron wire  $W$  which can be attracted by a magnet so as to touch the gold leaf system, and then allowed to fly back leaving the latter perfectly insulated. The gold leaves are then at the potential of  $E$

Since the latter remains at the same potential throughout, any leak across the sulphur plug will only tend to keep the deflection of the leaves at their original value. Any loss of charge must take place therefore across the gas. Even under these circumstances it was found that the leaves gradually became discharged, the loss of charge per second being about  $10^{-8} V$  electrostatic units of charge where  $V$  is the volume of the vessel.

We see therefore that even in its normal state a gas allows the passage of a small current of electricity. Under certain circumstances, however, the gas acquires a conductivity many times greater than the normal, and these currents have acquired considerable importance in the development of modern electrical theory.

If, for example, a quantity of radium is brought near the electroscope of Fig. 1, the leaves collapse with considerable rapidity and similar effects are observed if an X-ray tube is worked in the vicinity. Gases drawn from a Bunsen flame also possess temporarily the power to discharge a conductor, and this capacity is enormously increased if the flame is fed with a volatile salt such as sodium or potassium chloride.

The power to discharge a conductor persists in the gas for some little time after the active agent has been removed, and is transferred from place to place with the air. Thus if air from a Bunsen flame (Fig. 2) is drawn in a continuous current into an electroscope, the latter will be discharged.

If, however, the gas is filtered through tightly packed glass wool or passed through water the effect disappears, and it can also be removed by subjecting the gas to a strong electric field. It disappears spontaneously if the gas is allowed to stand for a few seconds

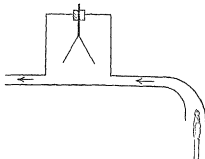


Fig. 2

### 5. Ionization theory of gaseous conduction.

The phenomena of the passage of electricity through gases can best

be explained by assuming that charged systems are set up in the gas by the action of the various agencies, and that these charged systems or gaseous ions, as they are called, convey the current across the gas by moving in opposite directions through the gas under the action of the electrostatic field set up by the charged body, in much the same way that a current is conveyed through the solution of an electrolyte by the motion of the positively and negatively charged electrolytic ions

Thus if the body has a positive charge and is surrounded by a gas containing gaseous ions the negative ions will be attracted to the body, and giving up their charges to it will gradually bring about its discharge. The difference between electrolytic and gaseous conduction which experimentally is very marked is due to two principal causes. In the first place the electrolytic ions are formed by the mere process of solution and persist so long as the salt remains dissolved, while the gaseous ions are only formed by the action of an external agency, which we may call the *ionizing agent*, and gradually disappear when the latter is removed. In the second place the number of charged systems present in a gas under the most intense ionizing agent is only a very small fraction of those present even in very dilute electrolytic solutions.

**6 Methods of measuring the current through a gas**  
 Before proceeding to describe the phenomena attending the passage of an electric current through gases it will be convenient to explain briefly the methods available for measuring such currents. The current through a normal gas is as we have seen about  $10^{-8}$  electrostatic units (e.s.u.) per unit volume. If the volume of gas is one litre this corresponds to a current of  $10^{-5}$  e.s.u., since current is the rate of flow of electricity. The current through the gas is thus equal to  $10^{-5}/3 \times 10^{10}$  in absolute electromagnetic units (e.m.u.), that is  $\frac{1}{3} \times 10^{-15}$  e.m.u. or about  $3.3 \times 10^{-15}$  amperes. This is at least ten thousand times smaller than the smallest current which could be detected on our most sensitive galvanometers. Thus even if the conductivity of the gas is increased a thousand fold by the ionizing agent the current will still be beyond the range of a galvanometer.

Let  $Q$  be the charge at any instant on an electrical conductor of capacity  $C$ . The potential of the conductor is given by the equation

$$Q = C V$$

The current  $i$  through the gas at any instant is given by the rate of loss of charge of the conductor. Thus

$$i = dQ/dt = C \cdot dV/dt \quad (1)$$

since the capacity  $C$  is constant

Thus if the rate of loss of potential can be measured, as for example by measuring the rate of collapse of the leaves of an electroscope, the current through the gas can be calculated when the capacity of the charged system is known. This method was employed by Wilson in his measurements on the conductivity of a normal gas already described.

In this form of measurement the potential across the gas must be adjusted to suit the instrument used. Thus if the gold leaf electroscope requires a potential difference of, say, 100 volts to produce a sensible deflection of the leaves we cannot work with potential differences of less than this amount. It is often, therefore, more convenient to measure the rate at which an insulated conductor receives electric charge from the gas under the action of a field supplied by another electrode immersed



in the gas. The current will again be measured by  $i = C \, dV/dt$  as before, where  $C$  is the combined capacity of the receiving electrode and the measuring instrument, and  $dV/dt$  the rate at which the potential of the latter increases.

**7. Measuring instruments** The instruments used in practice are either the Dolezalek electrometer or some form of

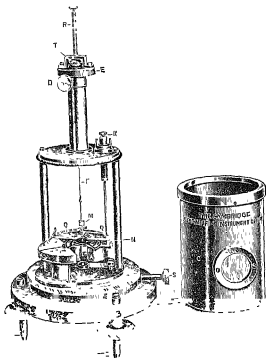


Fig 3

gold leaf electroscope. The Dolezalek electrometer (see Fig 3) is an improved form of the quadrant electrometer described in the text-books on electrostatics, in which special attention is paid to obtaining not only a high degree of sensitiveness but also a small capacity. The quadrants are small and are carefully insulated on amber supports. The needle is made as light as possible and supported by a fine strip of phosphor

bronze The instrument is used heterostatically, the needle being kept at a constant potential of about 120 volts by means of a cabinet of small accumulators. These cabinets are of the greatest service in work of this kind and generally consist of 500 cells arranged so as to give any voltage in steps of 2 volts up to a maximum of 1000 volts One pair of quadrants of the electrometer is connected to the electrode at which the current is to be measured, the other pair being permanently earthed. If the collecting electrode is initially earthed, the rate of increase of deflection of the needle is proportional to the rate of rise of potential of the insulated quadrants, that is, to  $dV/dt$ .

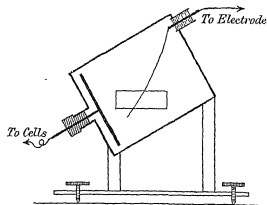


Fig 4

If the deflection is measured by a reflected beam of light in the usual way, a deflection of 1000 mm. per volt can be obtained on a scale placed one metre from the instrument. The capacity of the electrometer is generally of the order of 50 e.s.u.

**The gold leaf electroscope** One form of electroscope has already been described and is still largely employed for certain classes of measurement. A more sensitive form, also due to C. T. R. Wilson, is the tilted electroscope (Fig. 4). In this instrument the gold leaf which is initially at zero potential is attracted outward from the vertical position by a plate

which is charged to some constant potential, usually about 160 volts, by a cabinet of cells. If the plate is positively charged a small negative potential on the leaf will cause it to be attracted still further towards the plate, while a small positive potential will cause it to move towards the vertical position. The position of the gold leaf is read by a microscope with micrometer eyepiece. For certain potentials of the plate, and for a certain position of tilt of the instrument, generally about  $30^\circ$  as in the figure the leaf becomes almost unstable and in this state is very sensitive to slight changes in the potential. The best conditions can only be found by experiment, and the instrument needs an apprenticeship. In skilled hands however it is capable of very accurate results. A sensitiveness of 200 divisions per volt can be obtained, and the capacity can be made very small, it need not exceed one or two electrostatic units.

**Comparison of the relative sensitiveness of the electrometer and electroscope.** A comparison of the two instruments affords a useful exercise in the principles of the method of measurement. Let us assume that the electrometer gives a deflection of 1000 divisions per volt, and the electroscope 200, and that in each case a rate of deflection of one division in 10 seconds can be measured. In the case of the electrometer this corresponds to a value of  $dV/dt$  of  $10^{-4}$  volts per second. The capacity of the instrument is, say, 50 e.s.u., or since one farad or practical unit of capacity is equal to  $9 \times 10^{11}$  e.s.u. the capacity of our electrometer is  $\frac{50}{9 \times 10^{11}}$  or approximately  $6 \times 10^{-11}$  farads. The smallest current which can be measured with accuracy is therefore  $6 \times 10^{-11} \times 10^{-4}$ , that is  $6 \times 10^{-15}$  amperes.

For the electroscope the rate of change of potential is on the same assumptions  $1/2000$  volt per sec., while the capacity is, say, 2 e.s.u., or about  $2 \times 10^{-12}$  farads. The smallest measurable current is thus  $2 \times 10^{-12} \times \frac{1}{2000}$  or  $10^{-15}$  amperes. Thus, although the electrometer is more sensitive as regards potential, the electroscope is more sensitive to current, owing to its smaller electrostatic capacity.

8. **The ionization chamber.** The actual form of the vessel used for containing, and applying a field to, the gas varies very much with the nature of the effect to be observed. A suitable form for investigating the variation of current with potential, and for many other experiments in which the field needs to be definite, is shown in Fig 5

The gas under investigation is contained in a metal box which is connected to earth, thus serving to shield the electrodes *A* and *B* from any stray electrostatic field. For a similar reason the wire leading from the insulated electrode *A* to the electrometer should also be surrounded by an earthed metal tube (not shown in the diagram). The electrodes are placed parallel to each other a few centimetres apart, *A* is connected to one

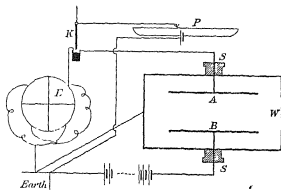


Fig. 5

pair of quadrants of an electrometer, or to the leaf of a tilted electroscope, and *B* is raised to any required potential by means of a cabinet of cells. The system *A* can be placed at zero potential by means of a key *K*, which can be earth-connected. When the key *K* is raised the system *A* is completely insulated, and begins to charge up with electricity of the same sign as the potential of *B*. If *K* is connected to a potentiometer, instead of directly to earth, the system *A* with its attached quadrants can be raised to a suitable known potential, and thus the electrometer can be calibrated, a process which needs to be repeated frequently with these sensitive instruments.

The ionizing agent may be enclosed in the box, but it is generally more convenient to have it outside, in which case a window  $W$  of some substance transparent to the ionizing rays, and generally consisting of a very thin sheet of aluminium foil, must be made in the side of the box. The electrodes are insulated from the box by insulating stoppers  $S, S$ . The insulation of  $A$  is very important, and should be of amber, sulphur, or quartz. The box and its electrodes forms what is known as an *ionization chamber*.

Suppose  $B$  is now raised to some constant potential, say, 200 volts positive, while  $A$  is earthed by the key  $K$ , and the gas exposed to the action of the ionizing agent. The ions in the gas begin to move under the action of the field between the plates, the positive towards  $A$ , the negative towards  $B$ . As long as the wire  $K$  remains in the mercury cup, the potential of  $A$  remains zero. As soon as it is withdrawn  $A$  begins to charge up positively, and the needle of the electrometer begins to move. Let  $t$  be the time taken for the needle to reach the deflection corresponding to a potential  $V$ . Then if  $C$  is the capacity of  $A$  and its connected quadrants, etc., the average current through the gas is given by

$$i = C \frac{V}{t}.$$

The actual potential corresponding to a given deflection can easily be found by lowering the key  $K$  again into the mercury cup, and sliding the end of the wire connected to  $K$  along the potentiometer wire until the deflection reaches the given value. The corresponding potential can then be read off on the potentiometer. For very accurate work, particularly with electroscopes, it is generally desirable to repeat this calibration after every reading.

9. **Variation of the current with the potential across the gas.** Suppose now the potential of  $B$  is gradually changed. For simplicity we will suppose that the maximum voltage acquired by  $A$  in charging up is not allowed to rise sufficiently to affect materially the potential difference between the plates. We can then study the magnitude of the current through the

ionized gas for different potential differences between the plates. In the case of a metallic conductor or of an electrolyte with non-polarizable electrodes, the relation is expressed by Ohm's law, that is, the current is simply proportional to the potential difference. The relation for a gas is, however, more complex, and is represented by a curve such as that of Fig. 6 which is plotted from an actual set of readings.

At first, and for very small voltages, say, less than one volt, the current is approximately proportional to the applied potential difference—that is at this stage the gas obeys Ohm's law, though probably not with the same degree of accuracy as a metallic conductor. As, however, the potential of  $B$  is

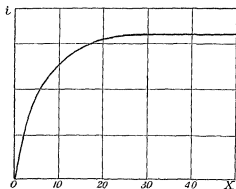


Fig. 6

raised above a certain value which depends on the nature and pressure of the gas, the distance apart of the electrodes and the intensity of ionization, a stage is reached when the current falls appreciably below the value which would be given by Ohm's law.

If the potential is pushed still higher a point is reached at which further increase in the potential of  $B$  produces no further increase in the current through the gas. After this point *the current is independent of the voltage*. This maximum current is called the *saturation current* through the gas, and the potential necessary to produce this current is known as the *saturation voltage*. The actual value of the saturation voltage depends

upon the distance apart of the electrodes, and the intensity of the ionization in the gas. Except in cases of very intense ionization, a field of from 20 to 30 volts per cm. between the electrodes is sufficient to produce the saturation current.

10. Variation of the saturation current with the distance between the electrodes, and the pressure of the gas. If one of the electrodes is made movable the variation of the saturation current with the distance apart of the electrodes can be studied. In the case of a metallic conductor the current for a given potential difference is inversely proportional to the length of the conductor, and a similar result holds for electrolytes. For gases however, if we arrange that the effect of the ionizing agent is the same in all parts of the gas, the saturation current through the gas is directly proportional to the distance apart of the electrodes. It can also be shewn, by using electrodes of different sizes, to be directly proportional to the area of the electrodes. If the pressure of the gas is varied it is found that the saturation current is directly proportional to the pressure of the gas. In other words *the saturation current through a gas is directly proportional to the mass of gas between the electrodes*.

The effects when the current is not saturated are in general very complex, and need not concern us here.

11. Theory of conduction through gases. Let us assume that the ionizing agent is producing ions uniformly throughout the gas and at a constant rate, so that  $q$  pairs of ions are formed per c.c. per second in the gas. These ions are charged positively and negatively, and since the gas as a whole is uncharged, the number of positive and negative systems must be equal, supposing that each carries a charge of the same magnitude  $e$ .

In general ions may be lost by the gas in three ways. In the first place since the ions are oppositely charged they attract each other according to the ordinary laws of electrostatics. On collision then charges may neutralise each other, and the ions return to their ordinary uncharged state. The chances of a given positively charged ion meeting a negative ion in a given

time is obviously proportional to the number of negative ions present per c.c., while the number of positive ions finding partners in a given time is proportional to the number of positive ions actually present per c.c. of the gas. The rate at which combination goes on is thus proportional to  $n^2$  where  $n$  is the number of ions of either sign present in unit volume of the gas. It can, therefore, be written  $an^2$  where  $a$  is a constant under given conditions and is known as the *coefficient of recombination*.

We have assumed that the numbers of positive and negative ions are equal. This is usually the case. If, however, for any cause they are different the rate of recombination by the same argument will be given by  $an_1n_2$ , where  $n_1, n_2$  are the number of positive and negative ions per c.c.

Ions are also withdrawn by the action of the electric field, and by diffusion to the electrodes or to the walls of the chamber. In general the effect of diffusion is small and may be neglected. In special circumstances it may become appreciable, and in these cases it can be measured.

Let us assume for a moment that there is no electric field across the gas and that the diffusion is negligible. Then the rate of increase in the number of ions per unit volume of the gas is equal to the number formed per second by the action of the ionizing agent less the number lost by recombination. Hence

$$\frac{dn}{dt} = q - an^2.$$

The ionization reaches a steady state when  $dn/dt$  is equal to zero or

$$q = an^2 \quad (2)$$

If the ionizing agent is then withdrawn  $q$  becomes zero, and the ionization in the gas decreases according to the equation

$$\frac{dn}{dt} = -an^2,$$

$$\text{or} \quad \frac{1}{n_0} - \frac{1}{n} = at, \quad \dots \quad (3)$$

where  $n_0$  is the value of the ionization at the moment when the agent was removed, and  $t$  the time which has elapsed.



12. Motion of the ions under a uniform electric field. If  $X$  is the strength of the electric field across the gas the force acting on any ion is equal to  $Xe$ . If the ion were perfectly free to move this would produce a constant acceleration of  $Xe/m$  where  $m$  is the mass of the ion. The ion is, however, moving through other uncharged gas molecules, its path therefore is made up of a series of short runs, each terminating in a collision in which all the accumulated energy of the ion is lost. Under these circumstances it is easy to shew that the ion will move not with a uniform acceleration but with a constant velocity which is proportional to the field applied.

For let  $\lambda$  be the mean free path of the ion in the gas, and  $\tau$  the time taken by the ion to describe its mean free path under the action of the field. We may suppose that the whole of the velocity added by the field is removed at each collision and that the ion thus starts its course again with zero velocity. Between two collisions the ion moves freely under the action of the field. If  $X$  is the intensity of the field and  $e$  the charge on the ion, the mechanical force is  $Xe$  and the velocity  $v'$  of the ion on reaching the end of its path is therefore given by  $Xe\tau = mv'$ ,

$$\text{or} \quad v' = \frac{Xe\tau}{m}$$

The average velocity with which the ion describes its path is thus  $\frac{1}{2}v'$ , and if we assume that the time occupied by a collision is small compared with  $\tau$ , this is also the mean velocity of the ion through the gas. The velocity of the ion is therefore given by

$$\frac{1}{2} \frac{Xe\tau}{m}, \quad \dots \quad (4)$$

and is thus directly proportional to the applied field  $X$ , since  $e$ ,  $m$  and  $\tau$  are constants under given conditions.

Thus if  $u$  and  $v$  are the actual velocities of the positive and negative ions respectively in a field of strength  $X$ , we have

$$u = k_1 X, \quad v = k_2 X,$$

where  $k_1$  and  $k_2$  will be constants for a given gas under given conditions of temperature and pressure. They are known as the *mobilities of the ions*

### 13. Theoretical relation between current and potential

Let us now consider the current through the gas due to an applied potential difference  $V$  between the electrodes. Considering any plane in the gas normal to the direction of the field, then in one second all the positive ions which are situated at a distance of less than  $u$  cm. from it will be driven across the plane, while similarly all the negative ions distant less than  $v$  cm. from the plane will be driven across it in the opposite direction. The total transference of electricity across the plane in unit time will be the sum of the charges carried by the two sets of ions. If the magnitude of the charge  $e$  carried by an ion is the same for all ions the total transference is thus  $ne(u+v)$  units per sq. cm. per sec. or if  $A$  is the area of the plane the total current across it will be

$$\begin{aligned} i &= Ane(u+v) \\ &= Ane(l_1 + l_2)X \quad . \quad . \quad (5) \end{aligned}$$

Now the passage of a current implies the withdrawal of a certain number of ions from the gas to the electrodes. The greater the current, the faster the ions will be removed, and hence the fewer will be the number of carriers left in the gas. Hence it is obvious that  $n$ , the number of ions present in unit volume of the gas, is a function of the current  $i$ . The problem is thus far from simple. We may however distinguish two limiting cases.

(1) *The current is so small that the number of ions withdrawn is negligible compared with the number present per c.c.* In this case the loss of ions is due solely to recombination and  $n$  is a constant, its value being given by (2).

If the electrodes are arranged so that the field is uniform, as for example in the case of two parallel plates, the field is equal to  $V/d$ , where  $V$  is the potential difference between the electrodes and  $d$  their distance apart. In this case equation (5) becomes

$$i = Ane(l_1 + l_2)X = Ane(l_1 + l_2)\frac{V}{d}, \quad (6)$$

where  $A$  is the area of either electrode. This equation is of the same form as that for conduction through an electrolyte, if  $n$  is a constant. Under these circumstances the current through

the gas obeys Ohm's law, and this case corresponds to the first straight portion of our experimental curve.

(2) *The field is so large that the ions are conveyed to the electrodes without appreciable recombination*

If the field is large the velocities of the ions become so great that the number recombining in the small time taken to reach the electrodes becomes negligible. In this case it is obvious that all the ions formed in the gas by the ionizing agent will be conveyed to one or other of the electrodes. If  $B$  is the volume of the gas between the electrodes the number of ions formed per second is  $Bq$  and the total charge conveyed to either electrode in one second is therefore  $Bqe$ . This is the maximum current through the gas, and, provided that the voltage is sufficient to produce saturation, is obviously independent of the difference of potential between the plates. This case therefore corresponds to the saturation current through the gas. It will be seen that the saturation current should be directly proportional to the volume of the gas, a result which we have already found experimentally.

Since the time taken for the ions to reach the electrodes is proportional to the distance which they have to travel, that is, to the distance apart of the electrodes, while the field for a given potential difference is inversely proportional to the distance between the electrodes, it follows that the potential necessary to produce the saturation current through the gas is directly proportional to the square of the distance apart of the electrodes. It has also been shewn to be proportional to the square root of the intensity of ionization.

Since the saturation current is found to be proportional to the pressure, it follows that  $q$ , the rate of ionization for a given strength of the ionizing radiation, is directly proportional to the pressure, that is to say, the number of ions formed is proportional to the number of molecules present.

(3) *The general case* has been considered by Sir J. J. Thomson, who found that on certain assumptions the current through the gas could be represented by an expression of the form

$$V = At + Bt^2, \dots \dots (7)$$

where  $A$  and  $B$  are complicated constants and  $V$  is the p.d. across the gas. This expression is found to express the intermediate portion of the experimental curve (Fig. 6) reasonably well. This part of the curve is of no practical importance except in the case of the currents through flames where the ionization is so intense that the maximum fields which we can apply are insufficient to produce saturation. We will therefore defer this case until the experimental results for flames have been described (§ 69).

## CHAPTER III

### THE PROPERTIES OF THE GASEOUS IONS

**14 Measurement of ionic mobilities.** The mobility of an ion is defined as its velocity in cm per sec under the action of an electric field of one volt per cm. Ionic mobilities may be measured in various ways, the most direct of which is that due to Rutherford

*Rutherford's method* (1) Two large metal plates were placed parallel to each other and 16 cm apart on insulating blocks

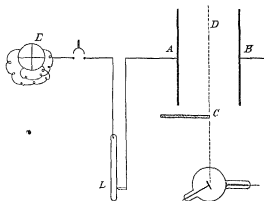


Fig 7

One of these, *B*, was connected to a battery so that any suitable field could be applied across the gas, the other, *A*, was connected through an insulated lever to an electrometer *E*

A heavy pendulum, not shown in the diagram (Fig 7), was arranged so that at one point of its swing it made the circuit of the primary of an induction coil the secondary of which was connected to the X-ray tube used for ionizing the gas. Rays

were therefore generated and the gas became ionized. After a given interval (which could be calculated from the time of swing of the pendulum and the distance apart of the switches) the pendulum swung against the lever  $L$  and so disconnected the plate  $A$  from the electrometer.

Owing to the screen  $C$  only the portion of the gas to the right of the plane  $CD$  is ionized. Hence to reach  $A$  the ions must travel through a distance equal at least to that between  $A$  and the plane  $CD$ . Hence unless the time taken by the ions to travel this distance is less than the time which elapses between the switching on of the rays, and the breaking of the electrometer circuit at  $L$ , the electrometer will shew no charge. If the time is gradually increased a point is reached when the electrometer begins to shew a deflection, that is when the ions from  $CD$  are just able to reach the plate  $A$  before the connection at  $L$  is severed. This critical time is evidently the time taken for the ions to travel under the action of the field from  $CD$  to  $A$ . In Rutherford's experiment the critical time was 0.36 sec., when the potential of the plate  $B$  was 220 volts and the distance to be travelled was 8 cm. The velocity of the ion was therefore 8/0.36 cm. per sec., with a potential gradient of 220/16 volts per cm. The mobility of the ions was therefore  $\frac{8}{0.36} \div \frac{220}{16}$  or about 1.6 cm. per sec. per volt per cm.

*Langevin's method of measuring mobilities* (2). Rutherford's method, though very direct, is not capable of great accuracy. It has been replaced by one due to Langevin. The gas, as before, is enclosed between two parallel plane electrodes and exposed to a suitable difference of potential, one of the electrodes being connected to a battery, the other to an electrometer.

In performing the experiment the connection with the battery is made and the *whole* of the gas between the plates is then ionized by a single instantaneous flash of X-rays from a powerful bulb. After some interval of time  $t$  from making the flash the direction of the field across the gas is reversed by reversing the potential of the charged electrode. The charge which has been received by the insulated plate is measured by the electrometer, and a curve is plotted shewing how this charge varies with the

interval  $t$  between the flash and the reversal of the field. This interval must, therefore, be variable and must also be capable of accurate measurement. In practice this can be effected by arranging that the various electric circuits are operated either by a pendulum, as in Rutherford's experiment, or more conveniently by a falling weight.

To simplify the problem we will assume that the times concerned are so short that we may neglect recombination. Let us assume that the charged plate is originally positive and that the strength of the field is  $X$ . As soon as the flash passes, ionizing the gas, positive ions begin to move towards the insulated plate with a velocity  $k_1X$ . Hence in the time  $t$  which elapses before the reversal of the field all the positive ions contained in a slab of gas of thickness  $k_1Xt$  cm. reach the insulated electrode and give up their charges to it. Hence if  $n$  is the number of ions per unit volume the total number of ions reaching the positive plate will be

$$N = nk_1XtA$$

where  $A$  is the area of the plate.

In the same time a number of negative ions equal to  $nk_2XtA$  will have been removed at the other electrode. The total number of negative ions left in the gas at the moment of reversal is therefore  $(nAd - Ank_2Xt)$  where  $nAd$  is the total number of negative ions originally present in the gas. On reversing the field all these ions will eventually reach the insulated electrode.

The total *negative* charge communicated to this plate is the difference between the negative and the positive charges. Thus if  $e$  is the charge on each ion, the charge on the plate at the end of the experiment will be

$$\begin{aligned} Q &= e(nAd - Ank_2Xt) - e(nk_1XtA) \\ &= Ae\{nd - nX(k_1 + k_2)t\} \end{aligned} \quad (8)$$

Hence starting with a very small value of  $t$ , the graph between  $Q$  and  $t$  will be a straight line, the negative charge decreasing, and finally giving place to a positive charge as  $t$  is increased.

Suppose now that the negative ions travel faster than the positive. As  $t$  is increased a stage will be reached when all the negative ions will reach the charged electrode, before the

field is reversed. If  $d$  is the distance between the plates this will obviously occur when  $k_2 X t$  becomes equal to or greater than  $d$ . After this point is reached no negative ions will reach the insulated plate the positive charge on which will, therefore, be equal to

$$Q - Ae (nk_1 X t) \quad (9)$$

The relation will again be linear but the inclination with the axes will be altered. There will thus be a sharp kink in the curve at the point where the two lines meet, and this kink obviously occurs at the point where

$$t = \frac{d}{k_2 X} \quad (10)$$

Since the velocity of the positive ions is less than that of the negative, there will still be positive ions between the plates

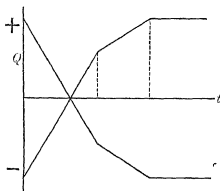


Fig. 8

when all the negative have been removed. If the reversal takes place before these have time to reach the insulated plate they will be carried back to the charged plate. Hence the charge on the insulated plate will still increase until the time between the flash and the reversal of the field is sufficiently long for all the positive ions to reach the insulated plate. This will occur when  $k_1 X t$  is equal to  $d$ , or

$$t = \frac{d}{k_1 X} \quad (11)$$

Since all the ions now reach the plate the total number reaching



the plate is simply equal to the number of positive ions formed by the rays, that is

$$Q = Aude$$

and is thus independent of the time

The complete curve between  $Q$  and  $t$  should thus have the form shewn in Fig 8, where the ordinates represent  $Q$ , and the abscissae the corresponding values of  $t$ . Since  $d$  and  $X$  are known, the times corresponding to the two kinks in the curve will give us the values of  $\lambda_1$  and  $\lambda_2$ .

Owing to want of uniformity in the ionization between the plates the experimental curves are not straight lines but have the form shewn in Fig 9 which is taken from one of Langevin's

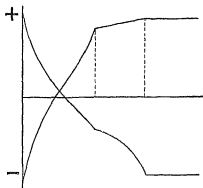


Fig 9

papers. It will be seen that the kinks are very pronounced, and the mobilities can thus be deduced with considerable accuracy.

**15. Mobilities of the ions in different gases** The following table (Table I) will give some idea of the mobilities of the positive and negative ions at ordinary temperatures and pressures. It will be noticed that for the lighter gases the negative ion has always a somewhat higher mobility than the positive. The difference becomes less as the molecular weight of the gas increases. It may be noted also that water vapour has in many cases a marked effect on the mobility of the ions, especially on the negative ions, the velocity of which it materially reduces. We shall return to these points later.

TABLE I

SUBSTANCE	$k_1 (+)$	$k_2 (-)$
Hydrogen	6.70	7.95
" (moist)	5.30	5.60
Air	1.36	1.87
" (moist)	1.36	1.61
Carbon monoxide	1.10	1.14
Carbon dioxide	.81	.85
Sulphur dioxide	.44	.41
Pentane	.35	.35

## 16. Approximate calculation of the mobility of an ion

We have seen, (4), p 19, that assuming that the ion retains none of the velocity produced in it by the field after collision with another atom, that its velocity through the gas is given by  $v = \frac{1}{2} \frac{Xc}{m} \tau$  where  $\tau$  is the time which elapses between two collisions. Now since the ion forms part of the gas it will participate in the thermal agitations of the gas molecules, and the kinetic theory shews that the kinetic energy of the ions for this motion must be equal to that of the molecules of the gas in which it is formed. This velocity will, therefore, vary as the square root of the mass of the ion. At ordinary temperatures these thermal velocities are very large. In the case of air for example the mean molecular speed at atmospheric pressure and 0° C. is 48,500 cm. per second. Since these velocities are distributed equally in all directions the number of ions carried by the thermal agitations across any plane in the gas in one direction will be equal to the number carried across it in the opposite direction, and hence the total transference of electric charge across the plane will be zero. Thus the thermal agitation causes no transference of electricity, and hence no current in the gas. We may, therefore, neglect it in considering the transference of electricity through the gas. On the other hand it will be the controlling factor in determining the number of collisions made by the ion. If  $\lambda$  is the mean free path of the ion in the gas, and  $V_1$  the velocity of the ion, then  $\tau$  the time occupied in describing the mean free path will be

equal to  $\lambda/V_1$ . But since the velocity of the thermal agitation is very large compared with the velocity added by the field (which in the case of a field as great as 100 volts per cm. would only amount to about 160 cm. per sec.), the value of  $V_1$  will be practically equal to  $V$  the velocity of the thermal agitation. Hence we have, on substituting for  $\tau$  in (4),

$$v = \frac{1}{2} \frac{e}{m} \frac{\lambda}{V} X \quad . \quad . \quad . \quad (12)$$

or the mobility of the ion is equal to  $\frac{1}{2} \frac{e}{m} \frac{\lambda}{V}$

This formula should enable us to calculate the mobility of an ion if the size of the ions is known, or conversely to deduce the size of the ion from its mobility. If we assume that the ion formed in, say, oxygen is simply a charged molecule of the gas, then  $V$  is the ordinary velocity of the oxygen molecule, or 461 metres per second: the value of  $e/m$  for a hydrogen atom, as we shall see later (§ 25), is  $10^4$  e.m.u. per gm., and for the oxygen molecule therefore, assuming that all ions carry the same charge, it is  $\frac{1}{16} \times 10^4 \lambda$ , the mean free path of an uncharged molecule of oxygen at normal temperature and pressure is  $10^{-6}$ . Substituting these values we have the mobility in oxygen equal to  $3.2 \times 10^{-8}$  cm. per sec. per absolute e.m.u. of field or 3.2 cm. per sec. per volt per cm. since a volt is  $10^9$  absolute e.m.u. of potential.

This is rather more than twice the measured mobility of the positive ion in oxygen, and would indicate that the ion is somewhat larger, but not much larger, than the molecule. In all probability it is identical with it. The formula we have developed above overestimates the mobility for two reasons. In the first place our assumption that no time is lost during collision is possibly not accurately true. In the second case the mean free path of a charged ion will certainly be less than the mean free path of an uncharged molecule of the same size on account of the electric attraction between the charge on the ion and the uncharged molecules of the gas. Hence we are led to the conclusion that in a gas at normal pressures the gaseous ion consists of a single molecule of the gas bearing an electric charge.

Although the theory outlined above has been challenged, it seems to be amply substantiated by the recent work of Loeb (3). He has shown, moreover, that the number of collisions which the free electron makes with neutral molecules before it succeeds in attaching itself to one of them varies with the chemical nature of the gas. In fact, in very pure hydrogen or nitrogen such attachment apparently never takes place and the electron remains in its free state. The corresponding negative mobilities are therefore much higher than for the gases in which attachment takes place, and are certainly greater than 750 cm per sec per volt per cm at atmospheric pressure. This inability of the hydrogen and nitrogen molecules to form negative ions has been noticed by Sir J. J. Thomson in his Positive ray experiments (§ 56).

#### 18 Measurement of the coefficient of recombination

The coefficient of recombination of the ions can be measured directly by a method due to Rutherford. A steady stream of gas is passed down a long tube (Fig. 11) at the entrance to which

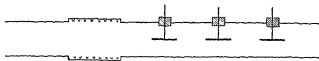


Fig. 11

is placed a layer of uranium oxide. This supplies a constant source of ionizing rays so that the gas is all ionized to the same extent. At various points along the tube are placed electrodes which can be connected to an electrometer. These electrodes may conveniently take the form of thin rods of equal length parallel to the axis of the tube, while the tube itself, raised to a sufficiently high potential to produce the saturation current through the gas forms the other electrode.

The saturation current is measured successively at each of the electrodes. Since the electrodes are all equal and similar the saturation currents will obviously be proportional to the number of ions present in the gas per unit volume, at the given electrode. If the distance apart of the electrodes is

known, and the rate of flow of the gas along the tube, the time taken for the gas to flow from one electrode to the next can be calculated, and thus the number of ions left in the gas after various intervals of time is obtained. In this way Rutherford was able to verify experimentally the equation (3) for the rate of decay of ionization in the gas. In one of his experiments, for example, he found that the ionization amounted to as much as 10 per cent of its maximum value as long as four seconds after removal from the ionizing rays, while in another experiment where the initial ionization was less intense the gas even after 16 seconds retained 10 per cent of its initial conductivity.

This method though simple, and direct, is not capable of any great accuracy, and has been replaced by one due to Langevin<sup>(1)</sup>, which however requires a knowledge of the mobilities of the ions under the conditions of the experiment. The gas to be experimented upon is contained between two parallel plates, *A* and *B* (Fig. 12), and a layer *CD* of it parallel to the plates is ionized by a single powerful flash of Röntgen rays. An electric field is applied between the plates by connecting one of them to a suitable number of cells, the other being connected to an electrometer in the usual way.

The ions begin to move under the field towards the opposite plates. All recombination must occur within the ionized layer. As soon as the ion leaves this layer it is surrounded only by ions of its own sign, and therefore cannot recombine. It is obvious that the faster we can pull the ions out of the layer the smaller the recombination will be, and the larger the charge we shall collect on the insulated plate, *A*.

Suppose that after an interval *t* there are in the ionized layer *n* positive and *n* negative ions per unit volume. The positive ions are moving with a velocity  $k_1X$  and the negative with a velocity  $k_2X$  in the opposite direction. The walls of the slab

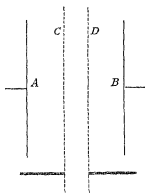


Fig. 12

are therefore approaching each other with a velocity  $(k_1 + k_2)X$ . Thus in a small time  $dt$  the thickness of the layer is reduced by  $(k_1 + k_2)Xdt$  and the number of ions of each kind separated is

$$n(k_1 + k_2)Xdt$$

Since the ions so separated are no longer liable to be lost by recombination, they will eventually reach the corresponding electrode giving to it a charge

$$dQ = en(k_1 + k_2)Xdt$$

But

$$n = \frac{n_0}{1 + n_0at},$$

where  $n_0$  is the number of ions of each kind originally present in unit volume,

$$\therefore dQ = \frac{(k_1 + k_2)n_0eXd}{1 + n_0at} \quad \dots \quad (13)$$

This process continues until the walls of the slab meet. If the thickness of the slab is  $d$  this obviously occurs when

$$t_1 = \frac{d}{(k_1 + k_2)X} \quad \dots \quad (14)$$

After this no recombination occurs. The total charge  $Q$  is therefore obtained by integrating between the limits  $t = 0$  and  $t = t_1$ .

Thus the total charge given to the plate

$$\begin{aligned} Q &= (k_1 + k_2)Xe \int_0^{t_1} \frac{n_0}{1 + n_0at} dt \\ &= \frac{(k_1 + k_2)Xe}{a} \left[ \log(1 + n_0at) \right]_{t=0}^{t=t_1} \\ &= \frac{(k_1 + k_2)Xe}{a} \log \left( 1 + \frac{n_0da}{(k_1 + k_2)X} \right). \end{aligned} \quad (15)$$

But  $n_0d$  is the total number of ions originally present and  $n_0da$  is thus the maximum charge  $Q_0$  obtainable when the saturation voltage is applied between the plates. This can easily be determined.

$$\begin{aligned} \text{Thus } Q &= (k_1 + k_2) \frac{Xe}{a} \log \left( 1 + \frac{Q_0a}{(k_1 + k_2)Xe} \right) \\ &= r \log \left( 1 + \frac{Q_0}{r} \right), \quad \dots \quad (16) \end{aligned}$$

$$\text{where } r = \frac{(k_1 + k_2)Xe}{a}.$$

Hence  $\alpha$  can be calculated, if  $k_1$ ,  $k_2$  and  $c$  are all known. This method gives very accurate results. The determination of  $c$ , the charge carried by an ion, is described in the next chapter.

The values found for  $\alpha$  vary very little in different gases. Air, oxygen, and carbon dioxide all give values of  $\alpha$  of about  $1.6 \times 10^{-6}$  at atmospheric pressure, and temperature. The value for hydrogen is  $1.4 \times 10^{-6}$ . The coefficient decreases as the pressure is reduced, and has only one-quarter of its normal value at a pressure of  $\frac{1}{2}$  atmosphere.

The number of collisions per second between uncharged molecules of oxygen is known from the kinetic theory to be  $1.25 \times 10^{10} n^2$  where  $n$  is the number of molecules per c.c. The number of recombinations occurring between oppositely charged ions in oxygen as determined above is  $1.6 \times 10^{-6} n^2$ . The number of collisions producing recombinations between the ions is thus about 10,000 times the total number of collisions which would occur in the same time between uncharged molecules of the gas. This must be due to the strong electrical attraction between the oppositely charged ions, which draws them together when otherwise they would never have met.

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## CHAPTER IV

### THE CHARGE ON AN ION

**19. Condensation of water drops on ions.** By applying a saturation voltage across a gas we can, as we have seen, sweep all the ions in the gas to one or other of the electrodes. The charge given to either electrode is then equal to the sum of the charges on all the ions of one sign present in the gas, that is, to  $ne$  where  $n$  is the total number of ions of either sign, and  $e$  the charge carried by each. To determine  $e$  it is necessary to find some method of counting the number of ions present in the gas.

A method of doing this was afforded by the discovery of C. T. R. Wilson that charged ions can serve as nuclei for the condensation of water vapour. It had long been known from the researches of Aitken that the water drops which form when a space becomes supersaturated with water vapour always collect about dust particles or similar nuclei present in the gas. If all nuclei are removed (either by filtration through cotton wool or better still by repeatedly forming clouds in the same closed space and allowing the drops so formed to settle, thus carrying the nuclei with them), a very considerable degree of supersaturation may exist in the gas without the separation of any drops. If, however, the pressure of the aqueous vapour in the gas exceeds about eight times its saturation pressure for the temperature of the experiment a fine drizzle sets in even in the absence of all nuclei.

Wilson shewed that if the gas was ionized deposition could take place in the absence of other nuclei, the ions themselves serving as nuclei about which the drops could form. It was found that deposition would take place on negative ions when the pressure of the aqueous vapour was four times the saturation value, and on the positive ions when it reached about six times that amount.



These effects are due to surface tension. It can be shewn that the vapour pressure over a convex surface of liquid is greater than that over a plane surface by  $\frac{\sigma}{\rho - \sigma} \frac{2T}{r}$  where  $\sigma$  is the density of the vapour,  $\rho$  that of the liquid,  $T$  the surface tension, and  $r$  the radius of curvature of the surface. If  $r$  becomes indefinitely small as would be the case for a drop starting from zero dimensions this excess of pressure would be infinite, and the drop would immediately evaporate. The nuclei, by providing surfaces of finite radius of curvature on which to condense, enable the drops to commence at a finite size, and hence to grow to visible dimensions even with a comparatively small degree of supersaturation. The drizzle which sets in when the supersaturation is eight-fold is probably due to deposition round molecules of vapour or gas.

The effect of giving a charge to the drop can most easily be discussed from the considerations of potential energy. The potential energy of a drop due to its surface tension is equal to its area multiplied by the surface tension, that is to  $4\pi r^2 T$ , and becomes smaller as the radius is decreased. Hence surface tension will tend to reduce the size of the drop, that is, to assist evaporation, since any system tends to reduce its potential energy to a minimum. On the other hand the potential energy of a drop due to a charge  $e$  upon it is  $\frac{1}{2} \frac{e^2}{r}$ . This increases as  $r$  becomes smaller, and hence the effect of the charge is to tend to increase the size of the drop. The electric charge therefore acts in the opposite sense to the surface tension, and may be regarded as producing a diminution in it. Thus a charged drop will grow under conditions under which an uncharged drop of the same radius would evaporate. It is obvious, therefore, that a drop will be formed around a charged molecule, or ion, with a smaller degree of supersaturation than that required when the molecule is uncharged.

**20 C. T. R. Wilson's cloud experiments.** The method adopted for producing supersaturation in the air is based on the cooling of a gas by adiabatic expansion. The apparatus used

is shewn in Fig. 13. The gas in the expansion chamber is shut in by a movable piston *P*, which is made as light as possible so as to move with ease and rapidity. The joint is made air-tight with water *W*, which also serves to keep the space saturated with moisture. The air space inside the hollow piston communicates by means of a wide tube *T* with the barrel *B*, and the piston can be raised to any required position in the outer glass cylinder *D* by forcing a little air in through the tap

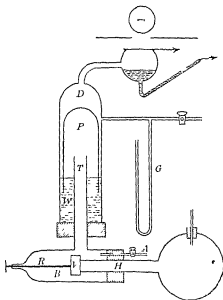


FIG. 13

*A*. Thus by suitably adjusting the initial position of the piston an expansion of any desired amount can be made.

The expansion is made as follows. A wide tube *H* connects *B* with a large vessel of several litres capacity which is kept at a low pressure by the continuous action of a water pump. *H* is normally closed by a valve *V*, but by smartly pulling back the rod *R* the valve is opened allowing the space beneath the piston to be exhausted very quickly through the tubes *T* and *H*. The pressure below *P* being thus reduced, it falls with

great rapidity, producing a nearly instantaneous expansion of the gas in the expansion chamber

The actual expansion can easily be deduced by reading the pressure gauge  $G$  before and after the experiment. Let  $\pi$  be the atmospheric pressure and  $p_1$  the difference of pressure in the two arms of the gauge before expansion. Then  $P_1$  the initial pressure of the gas in the chamber is  $(\pi - p_1 - \sigma)$  where  $\sigma$  is the saturation pressure of aqueous vapour at the temperature of the experiment. The final pressure of the gas after the apparatus has again attained the temperature of the laboratory is  $(\pi - p_2 - \sigma)$  where  $p_2$  is the new reading of the gauge. Hence by Boyle's law

$$\frac{v_2}{v_1} = \frac{\pi - p_1 - \sigma}{\pi - p_2 - \sigma},$$

which gives the expansion

Since the expansion of the gas is adiabatic,  $\theta v^{\gamma-1}$  is a constant

and

$$v_1^{\gamma-1} \theta_1 = v_2^{\gamma-1} \theta_2,$$

$$\log_e \frac{\theta_1}{\theta_2} = (\gamma - 1) \log_e \frac{v_2}{v_1} \quad . \quad . \quad (17)$$

which gives  $\theta_2$  since  $\gamma$  is known. The values of the saturation pressure of aqueous vapour at the temperatures  $\theta_1$  and  $\theta_2$  can be ascertained from tables and hence the degree of supersaturation produced in the space by the expansion can be obtained

Working with this apparatus Wilson (1) found that, after freeing the chamber from dust nuclei no cloud was formed for values of  $v_2/v_1$  less than 1.375, which was the expansion necessary to produce eight-fold supersaturation. If, however, the gas was previously ionized by passing X-rays into it through an aluminium window, a dense cloud appeared when the expansion exceeded 1.26, shewing that fresh nuclei are formed in the gas by the action of the rays. If these nuclei are gaseous ions they should be removable by the action of an electric field. This was found to be the case.

The effect of each kind of ion separately was investigated with a cloud chamber of the form shewn in Fig. 14. The chamber was divided by a central metal partition  $C$  which was earthed

and the two electrodes were charged positively and negatively respectively. The gas was ionized by a narrow pencil of rays close to each side of *C*. By the action of the two fields the positive ions in *A* and the negative in *B* were driven into the plate *C* so that all the ions in *A* were negative, and those in

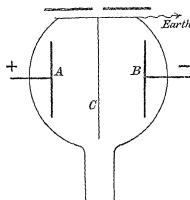


Fig 14

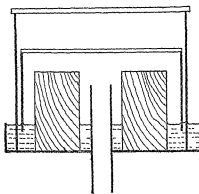


Fig 15

*B* positive. On making an expansion it was found that a cloud was formed as before on the negative ions when the expansion reached 1.26, but that no cloud appeared on the positive ions in *B* until the expansion reached 1.30, corresponding to a six-fold supersaturation. The negative ions are thus more efficient in condensing drops of water than the positive



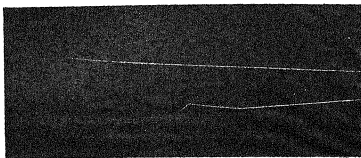


Fig 16



Fig 17



Fig 18

[To face page 41

### 21 C. T. R. Wilson's later condensation experiments

In the form of cloud chamber originally used the gas expanded through a side tube, and air currents were thus set up in the chamber. By modifying the apparatus so that the piston formed the floor of the cloud chamber itself (Fig. 15) it was found possible to produce expansion while leaving the gas perfectly at rest (2). The expansion arrangements were otherwise unaltered. By allowing one or two ionizing particles to enter the chamber and producing a simultaneous expansion in the air the track of the particle through the chamber was rendered visible by the drops formed round the ions produced along its path. Fig. 16 shews a photograph of the tracks made by  $\alpha$ -particles from radium. The ionization caused by the  $\alpha$ -particles is so intense that the drops coalesce into a single continuous streak. Fig. 17 in the same plate shews the track left by a single  $\beta$ -particle. Here the ions formed per cm. are far less numerous than in the case of the  $\alpha$ -particle and the individual ions can be clearly seen. Fig. 18 is a photograph of the track left by a beam of X-rays passing from left to right. We shall refer to this later. The method is proving of great importance in the study of the properties of ionizing radiations (3).

**22 Application of the condensation experiments to the determination of  $e$  Thomson's method (1)** Suppose a cloud is formed in a cloud chamber of the form in Fig. 13, the expansion being arranged so that the drops condense only on the negative ions in the gas. These ions may be produced by any convenient ionizing agent. Let  $W_1$  be the weight of water vapour required to saturate the space inside the chamber completely at the initial temperature, and  $W_2$  that required to saturate it at the lowest temperature reached during expansion. Then the weight of water deposited is given by  $M = W_1 - W_2$ , and is known since  $W_1$  and  $W_2$  can be calculated from the volume of the chamber and the densities of the saturated vapour at the two temperatures. It may be assumed that, providing that drops are formed, the whole of the vapour over and above that required to saturate the space will be deposited.

The small drops making up the cloud will fall under the action

of gravity with a uniform limiting velocity given by Stokes' law. Thus if  $r$  is the radius of the drop,  $\eta$  the viscosity of air,  $\rho$  the density of water, and  $g$  the acceleration due to gravity, the drops will fall with a uniform velocity given by

$$v = \frac{2}{9} \frac{g\rho r^2}{\eta} \quad . \quad . \quad . \quad (18)$$

This velocity can be measured by observing the rate at which the surface of the cloud settles down by means of a cathetometer or reading microscope. Since all the constants are known the observed value of  $v$  will enable us to calculate the radius  $r$  of a single drop. It is found that the drops are all the same size, as can be seen from the fact that the cloud settles down as a whole without separating into layers. The mass of each drop is therefore  $\frac{4}{3}\pi r^3\rho$  and if  $n$  is the total number of drops in the cloud

$$\frac{4}{3}\pi r^3\rho n = M \quad . \quad . \quad . \quad (19)$$

which gives us  $n$  since  $M$  the mass of the cloud is known.

If the water surface is connected to an electrometer the quantity  $Q$  of electricity brought down by the cloud can be measured. The charge on a single ion is then equal to  $\frac{Q}{n}$ .

*Balancing method of determining  $e$*  The previous method was first carried out by Sir J. J. Thomson. An interesting modification is due to H. A. Wilson (5). In this the clouds were formed and the radius of the drops determined by the application of Stokes' law as in the previous experiment. An electric field,  $X$ , was then applied across the chamber so as to attract the drops towards an upper plate which was positively charged, the lower surface being earthed. The electric force  $Xe$  acting on the drops was thus in the opposite direction to that of gravity, and by suitably adjusting the strength of the field the two forces could be made to neutralize each other exactly so that the cloud remained stationary in the chamber, suspended in air "like Mahomet's coffin." When this state is reached we have

$$Xe = mg \quad . \quad . \quad . \quad (20)$$

where  $X$  is the electric field and  $m$  the mass of the drop. But  $m$  can be calculated, as before, from the velocity of the free



fall under gravity and hence  $e$  can be obtained. Assuming that each drop forms round a single ion this is the charge on the ion.

Both these experiments are subject to a serious error. The gas after expansion begins to warm up again by conduction and radiation from the room, and consequently the space around the drops soon ceases to be saturated. Hence the drops begin to evaporate and their mass  $m$  is constantly decreasing during the course of the experiment. This defect has been overcome by a method due to Millikan.

**23 Millikan's experimental determination of  $e$**  The question has been investigated very fully by Millikan (6) using a

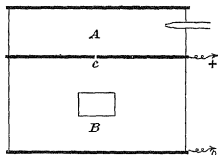


Fig. 19

method similar to that of Wilson but free from the uncertainties caused by evaporation. Instead of condensing drops of liquid on the ions Millikan forms his drops mechanically by some form of sprayer in an atmosphere saturated with the liquid, and leaves them to acquire charges from the ionized air by collision with the ions. His apparatus is shown in Fig. 19.

A little of the liquid under experiment, generally oil or mercury, was sprayed into the upper chamber  $A$ , and a few drops fell through a small hole  $c$  into the experimental chamber  $B$ . The upper and lower plates bounding this chamber were insulated and could be charged to varying differences of potential by a battery of small cells, so that any required vertical field could be applied across the gas, or by

connecting the plates together the field could be removed and the drop allowed to fall freely under gravity. Its radius could thus be deduced from Stokes' law, and knowing its density the mass  $m$  could be calculated. The drops showed little tendency to evaporate and the mass  $m$  remained appreciably constant over long intervals. By adjusting the field the drops could be made to remain stationary and a single individual drop could thus be kept under continuous observation for several hours.

Now the drops are not initially charged but if the air is ionized they become so by collision with the charged ions. Since the diameter of the drop is large compared with that of an ion, its potential rises comparatively slowly, and it may accumulate a considerable number of charges of the same sign before its potential becomes sufficiently high to prevent other like charges from reaching it. Thus the charge  $E$  on the drop at any instant may be any not too great integral multiple of the ionic charge  $e$ . On the other hand if an ion of opposite sign reaches the drop part of its charge will be neutralized and  $E$  will be diminished again by some multiple of  $e$ .

The drops can be observed by a microscope focused on them through a small window in the side of the chamber  $B$ . A drop is now singled out and its mass determined by observing its velocity of free fall under gravity by means of a vertical scale in the eye-piece of the microscope. A field is then applied and adjusted until the drop remains stationary. The charge on the drop can then be calculated from the strength of the field. If the drop is kept under observation it will be found that sooner or later the stationary balance is destroyed and the drop either darts upwards, shewing that it has acquired an additional charge of like sign, or begins to fall shewing that part of its charge has been neutralized. The field is adjusted again until a fresh balance is obtained and the new value of the charge  $E$  is calculated. If all ionic charges have the same magnitude, each of the charges so determined must be some not too large multiple of the ionic charge. The greatest common factor of all the observed values is thus the minimum ionic charge.

A very large number of charges were thus measured by Millikan using drops of various sizes and various liquids, and

also with different ionizing agents. In every case the charge was found to be a multiple of the number  $4.774 \times 10^{-10}$  e.s.u. to a very considerable degree of exactness.

In order to ensure the greatest accuracy possible various subsidiary experiments were made. For example, a fresh determination of the viscosity of air was made, an error of 2 per cent being found in the generally accepted value. Experiments were also made to test the applicability of Stokes' law in the case of the drops used, and a small correcting factor was found to be necessary, and its magnitude determined. This correction has since been shown to be required by a more rigorous mathematical analysis of the case of falling drops. Millikan claims that his result is not in error by more than one part in 1000.

These results of Millikan bring out very clearly the fact that electricity like matter is not indefinitely divisible but consists of units or "atoms" which cannot be further subdivided. In every case, no matter what was the ionizing agent used to produce the charges, no matter what the gas in which they were produced, or the nature of the drops on which they were measured, the observed charge was invariably a multiple of the value  $4.774 \times 10^{-10}$ , no fraction of this amount ever being observed. On the explanation given of ionization this charge is that carried by an electron if negative or due to the absence of an electron if positive. The electron, therefore, constitutes an atom of electricity. We shall, therefore, refer to this charge as the *electronic charge*, and denote it by the letter  $e$ . Millikan's experiments shew, and many other observations confirm it, that the charge carried by all electrons is the same. It is a real universal constant. Moreover, in many cases, the drops falling into the observation chamber were found to be already charged, by friction between the drop and the sprayer. These charges were also found to be integral multiples of  $e$ . Thus an ordinary frictional charge is also made up of electrons.

In nearly every case observed it was found (7) that when charges were gained or lost by the drop, owing to collision with a gaseous ion, the magnitude of the charge so interchanged was the single electronic charge  $e$ . Thus it appears that, in general, a

gaseous ion carries only a single electronic charge  $e$ , as we have previously assumed. The only exception was when the drops were surrounded by an atmosphere of helium, and the ionization was produced by  $\alpha$ -particles. In this case (8) about 16 per cent of the encounters resulted in adding a charge of  $2e$  to the drop, and thus about 16 per cent of the helium ions must be doubly charged. We must suppose that in this case about  $\frac{1}{6}$ th of the encounters between the  $\alpha$ -particles and the helium atom result in the ejection of two electrons from the atom. Apparently in all other cases ionization is produced by the ejection of a single electron only.

#### 24 Perrin's determination of $e$ from the Brownian movement.

When a current is passed through a solution of an electrolyte, the mass of the substance deposited on either electrode is proportional to the quantity of electricity which has passed. Thus the mass of hydrogen liberated by the passage of unit electromagnetic quantity of electricity is  $1.04 \times 10^{-4}$  gm (the electrochemical equivalent of hydrogen), in other words

one gram of hydrogen is in electrolysis associated with  $\frac{1}{1.04 \times 10^{-4}}$

or 9650 e.m.u. of charge. It is assumed that the ions in electrolysis are atoms of the substance carrying a charge  $E$  which is the same for all monovalent ions. Thus, if  $n$  is the number of atoms in one gram of hydrogen, and  $E$  the charge on each in solution in e.m.u., the total charge carried by one gram of hydrogen will be  $nE$ , which must equal the value 9650 as determined above. Since there are two atoms of hydrogen in a molecule, and a gram-molecule of hydrogen weighs 2 gm, we can also write this result in the form

$$NE = 9650$$

where  $N$  is now the number of molecules in a gram-molecule of gas, an important number known as Avogadro's constant. If we can determine  $N$  we can calculate  $E$ .

An interesting method of determining  $N$  is afforded by Perrin's (9) experiments on the Brownian movement.

Suppose a small particle, not too small to be visible with a powerful microscope yet not too large in comparison with the size of the molecules to be affected by collision with them, is suspended in water. This particle will, by the kinetic theory, be bombarded on all sides by the molecules of the water moving under their velocities of thermal agitation. On an average the number striking the particle will be the same in all directions and the average momentum communicated to the particle in any direction will be zero. Since, however, the collisions are governed by the law of probability there will, if the interval of time considered be sufficiently small, be an excess of momentum in one direction or the other, and if the mass of the particle is not too large compared with the masses of the colliding molecules it will be given an irregular kind of motion which may be observed under a microscope.

This motion has been known for many years as the Brownian movement and is always to be observed in suspensions of fine particles in a liquid.

Experiments have shown that the Brownian movements are independent of any currents in the liquid, or of any external vibrations. They occur with particles of any nature providing that the size is suitable, and they do not diminish with lapse of time. For example, Brownian movements can be observed among the fine particles enclosed in those liquid cavities which are often found in specimens of quartz and which have been sealed up for many millions of years. The explanation just given is the only one consistent with all these facts.

The particles in Brownian movement are thus sharing the thermal agitations of the molecules of the surrounding liquid in exactly the same way that the molecules of a heavy vapour share the motion of the molecules of a light gas in which they may be placed. In other words, from the point of view of the kinetic theory the particles in a suspension behave like the molecules of a dilute gas of very high molecular weight, each particle functioning as a single molecule. We can, therefore, apply the gas laws to them, and from observations on these visible particles determine the various unknown constants in the gas equations.

*Distribution of the particles in a suspension in a vertical direction when in equilibrium under gravity.* The most direct method of applying this result is to determine the way in which the particles of a suspension distribute themselves under the action of gravity. The case is similar to that of a gas under gravity.

Consider two horizontal planes separated by a distance  $dh$  in a vertical column of gas of unit cross section. If  $p$  and  $p + dp$  are the pressures at the two planes, the difference  $dp$  is equal to the weight of the gas enclosed between the two planes, since the cross section is unity. Hence if  $\rho$  is the density of the gas

$$\begin{aligned} dp &= mg = \rho g \, dh \\ &= \frac{M}{V} g \, dh \end{aligned}$$

where  $M$  is the molecular weight of the gas in grams and  $V$  is the volume of one gram-molecule. But  $V = RT/p$  where  $T$  is the absolute temperature and  $R$  is the gas constant. Thus

$$\begin{aligned} dp &= \frac{Mgp}{RT} dh, \\ \log_e \frac{p_0}{p} &= \frac{Mg}{RT} H. \end{aligned} \quad (21)$$

where  $H$  is the vertical distance between the two points in the vertical column where the pressures are  $p_0$  and  $p$ .

But the pressure is directly proportional to the number of molecules per c.c. in the gas. Hence we may write (21) in the form

$$\log_e \frac{n_0}{n} = \frac{MgH}{RT} \quad (22)$$

which gives the distribution of the molecules in a vertical column of the gas.

We can now apply this result to the case of the suspension. In this case if  $m$  is the mass of a single particle the "molecular weight in grams" will be equal to  $mN$  where  $N$  is the number of molecules in one gram-molecule of a gas, which by hypothesis is the same for all gases. The apparent mass of a particle suspended in a liquid is, however, less than its true mass  $m$  by the weight of the liquid it displaces; that is, it will be equal to

$$m \left( \frac{D-d}{D} \right),$$

where  $D$  is the density of the particle and  $d$  that of the liquid. Hence substituting in equation (22), we have

$$\log \frac{n_0}{n} = \frac{Nm}{RT} \left( 1 - \frac{d}{D} \right) gH. \quad (23)$$

If the mass of the particles and their density are known a determination of the ratio of  $n_0/n$  for different depths will enable us to calculate  $N$ , the constant of Avogadro.

A suitable emulsion was found in gamboge, the particles being obtained of uniform size by centrifugal fractionation. The density could be determined by finding some solution in which the particles would remain suspended without falling, while the volume could be determined either by direct measurement of the radius of the particle or by calculating the latter from its rate of fall under gravity by Stokes' law.

To find the vertical distribution of the particles when in equilibrium a small drop of the emulsion was placed in a hollow cut out in a micro-

scope slide (Fig. 20) and covered with a thin cover slip to prevent evaporation. A high power microscope was then focused on some definite layer of the emulsion and the field of view

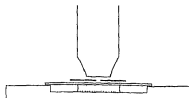


Fig. 20

limited by a stop so that not more than five or six grains were in the field of view at the same instant. Owing to the Brownian movement the particles are constantly appearing and disappearing but if not more than five or six are visible at the same time a practised eye can immediately grasp the number present at any given moment. Readings were made at equal short intervals of time, and the average number present in view is taken as proportional to  $n$  for that layer. Thus for some particular layer  $A$  in one set of experiments the numbers visible at ten successive moments were

2, 2, 0, 3, 2, 2, 5, 3, 1, 2,

giving an average of 2.2. At some higher level  $B$  the first ten readings were

2, 1, 0, 0, 1, 1, 3, 1, 0, 0,

giving an average of 0.9. The ratio  $n_1/n_2$  for these two layers was therefore 2.2/0.9. In this way the average number of particles occurring at different depths in the liquid was determined and was found to agree very closely with the theoretical distribution, as calculated above. Substituting the experimental values in equation (23)  $N$  was found to be  $68.2 \times 10^{22}$ . A second method based on the distribution after a definite interval of time in a horizontal plane of a number of particles introduced at a given point in the liquid gave a mean value of  $N = 68.8 \times 10^{22}$ . Substituting these results in the equation  $NE = 9650$  we find that the value of  $E$  the charge on a hydrogen ion in electrolysis is equal to  $1.40 \times 10^{-20}$  e.m.u. of charge or  $4.2 \times 10^{-10}$  e.s.u.

**25. Summary of results** The value obtained by Perrin for the charge on a monovalent ion in solution is sufficiently close to the value obtained by Millikan for the charge on a gaseous ion to make it reasonably certain that in each case the charge with which we are dealing is the unit electronic charge  $e$ . The agreement, however, is not as close as might have been expected. Millikan claims an accuracy of one part in 1000 for his own experiments, and Perrin considers that the error in his cannot be more than 3 per cent. On the other hand the difference between the two values is nearly 15 per cent. Perrin believes that the correction applied to Stokes' law in Millikan's experiments was insufficient, and that consequently the mass of his drops was wrongly estimated. If their size is sufficiently reduced, the oil drops employed by Millikan show Brownian movements, which at low pressures are very much larger than those shown by suspended particles in water. The actual displacements of these drops can easily be measured and are found to agree exactly with the theoretical laws governing the effect. The value of  $N$  deduced from these measurements (10) was  $60.3 \times 10^{22}$ , thus giving a value of  $e$  very close to that of Millikan. As, however, Stokes' Law is used in finding the mass of the drop, this hardly provides independent confirmation of this value. More recent experiments on emulsions in water have given values very close to Millikan's, which is also in close agreement with the values of  $e$  obtained by experiments on the  $\alpha$ -particle (§ 103) and with that deduced by Planck from the



TABLE II  
The charge on an electron

OBSERVER	METHOD	$e$ in e.s.u.
Beckman	Water drops (original method of Thomson)	$1.67 \times 10^{-10}$
Millikan	Oil and mercury drops	$4.774 \times 10^{-10}$
Perrin	Brownian movements	$1.2 \times 10^{-10}$
Rutherford	Charge on $\alpha$ -particle	$1.65 \times 10^{-10}$
Regener	" "	$4.79 \times 10^{-10}$
Planck	Theory of radiation	$4.69 \times 10^{-10}$

theory of radiation. The various results are given in Table II. In the present volume we shall assume,

$$e = 4.774 \times 10^{-10} \text{ e.s.u.} \\ = 1.591 \times 10^{-20} \text{ e.m.u.}$$

Assuming this value for  $e$  the value of Avogadro's constant becomes  $60.6 \times 10^{22}$  molecules per gm. molecule. Since the ratio of the mass to the charge for a hydrogen ion in solution (i.e. the electrochemical equivalent of hydrogen) is  $1.04 \times 10^{-4}$  e.m.u. per gm., the mass of a hydrogen ion in electrolysis is  $(1.04 \times 10^{-4}) \times (1.59 \times 10^{-20})$  or  $1.66 \times 10^{-24}$  gm. If the electrolytic ion is an atom of the substance, as is generally assumed, this is the actual mass of a hydrogen atom. The masses of other atoms can be obtained by multiplying this number by the corresponding atomic weight.

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## CHAPTER V

### IONIZATION BY COLLISION THE SPARK DISCHARGE

26. **Ionization currents with large voltages.** We have already seen (§ 9) that the current through an ionized gas increases with increasing electric field up to a certain maximum value known as the saturation current. There is then a considerable range of electric fields greater than this saturation value for which increasing the field produces no appreciable increase in the current. It is found, however, that if the field is increased above a certain value the current again begins to increase,

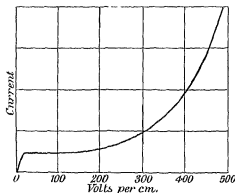


Fig. 21

at first slowly but soon with great rapidity (Fig. 21) until finally a spark passes between the electrodes, accompanied by a temporary but very considerable current. The field  $X$  required to produce an appreciable increase in the current above its saturation value depends on the distance apart of the electrodes, and on the nature and pressure of the gas. For air at ordinary pressures, and with distances of half a centimetre or more between the electrodes it is very large. It diminishes, however, as the pressure of the gas is reduced, and the phenomena are

most conveniently investigated in the case of gases at the comparatively low pressures of from one to ten millimetres of mercury. With such pressures it is possible to produce a considerable increase in the current through the gas with potential differences of not more than 50 volts.

The effect is to be ascribed to collision between the ions generated in the gas and the molecules of the gas. We have already shewn (§ 16) that the velocity acquired by an ion of mass  $m$  and charge  $e$  moving under the action of a field of strength  $X$  between two successive collisions is

$$\frac{Xe \lambda}{m V}$$

where  $\lambda$  is the length of the free path of the ion. Its velocity, on striking another molecule of the gas, is thus, for a given field, proportional to its free path.

The mechanism of ionization is a little obscure. Since however it involves the complete separation of a negative from a positive charge it is obvious that work must be done on the molecule so ionized, and the energy for this must be supplied by the source of ionization. In what follows we assume that this energy is supplied by the kinetic energy of the colliding particle. The kinetic energy of this particle must, therefore, reach a certain minimum value if fresh ions are to be produced by it in the gas by the process of collision.

The mean free path of a particle in a gas can be calculated from the kinetic theory of gases. The same theory, however, shews that in a considerable number of cases collision will not occur until the particle has described a free path considerably longer than the mean, while in others collision takes place before the mean free path has been described. Thus it can be shewn that in 14 per cent. of the total number of collisions collision will not occur until the particle has described a path at least twice as great as the mean, while in 10 per cent. of the cases it takes place before one tenth of the mean path has been completed. Thus assuming that the particle must describe a path  $\lambda$  before it has sufficient kinetic energy to produce fresh ions, ionization by collision will commence long before the mean

path of the ions has reached this critical value, and will not be complete until the conditions in the gas correspond to a mean free path considerably greater than the critical value.

**27. Difference in the effects produced by positive and negative ions** It is found by experiment that the negative ion is much more efficient in producing ionization by collision than the positive ion, and begins to do so for much smaller values of the field. Consequently under ordinary circumstances the increase in the current across a gas caused by increasing the field above the critical value is due almost entirely to the ionizing action of the negative ions. Since the mean free path of a particle is inversely proportional to the pressure of the

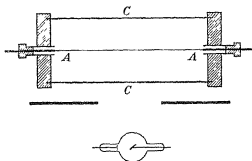


Fig. 22

gas the critical ionizing velocity is much more readily attained at low pressures than at high, and experiments on ionization by collision are most conveniently performed at pressures of the order of a few millimetres of mercury. At these pressures as we have seen the negative ion is identical with the electron, and has a much greater mobility than its positive partner. It is to this greater mobility that its superior efficiency is to be ascribed.

The difference in ionizing power can easily be demonstrated by experiments in which the field between the electrodes is not uniform but variable, as for example in the case where the field is set up between a central thin wire *A* and a coaxial cylinder *C* (Fig. 22). The field in this case is inversely propor-

tional to the distance from the axis, and is thus intense near the wire and very small near the cylinder. If air at ordinary pressures is enclosed in the cylinder, the saturation current is obtained with a difference of potential of a few hundred volts, and is independent of the direction of the field. It may be pointed out that owing to the want of uniformity of the field a much higher difference of potential is required to produce saturation in cylindrical ionization chambers of this kind than in those having parallel plate electrodes.

At low pressures a different state of affairs prevails. If X-rays are used as the ionizing agent it is known that the bulk of the ionization at low pressures is due to electrons emitted by the metal cylinder. The ionization produced in the gas by the

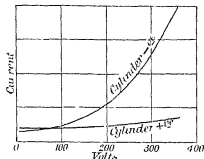


Fig. 23

direct action of the rays decreases proportionately to the pressure, while the number of electrons produced from the wire is small owing to its small surface. We may, therefore, regard the ionization as practically confined to the space near the walls of the outer cylinder.

If now the outer cylinder is positively charged the negative ions will be attracted to the cylinder and reach it after passing through a very small distance of air. The positive ions will be driven across the vessel to the wire.

If the field is reversed the opposite will be the case, the positive ions being withdrawn and the negative driven across the chamber.

Since the velocity in collision is proportional to the field,

ionization by collision will be confined, under the conditions of the experiment, to the space near the central wire where the field is strong, and will thus be due entirely to ions of the sign driven across the chamber. We can thus study the effect of each kind of ion separately. The results of such an experiment are shown in Fig. 23 where the lower curve refers to the positive ion and the upper to the negative. It will be seen that the positive ions produce no increase in the saturation current across the chamber at any rate until the voltage exceeds 350 volts. The negative however produce an appreciable increase in the current with a voltage as low as 100 volts. Thus until the field is very large ionization by collision is due almost entirely to the action of the negative ions in the gas.

28. **Expression for the current through the gas when ionization by collision occurs.** Confining our attention for the moment to the case where the ionization by collision is produced only by negative ions, let us consider the current between two parallel plates separated by  $d$  cm. of gas. Let  $n_0$  be the number of ions generated per cubic cm. of gas by the ionizing agent at a distance  $x$  from the positive electrode. Let  $\alpha$  be the number of ions which a single negative ion produces by collision in 1 cm. of its path.  $\alpha$  will depend on the field and on the mean free path, but will be constant under the conditions of any one experiment. Then assuming that the ions so formed will in turn produce fresh ions by their collision the number of ions generated by collision in a distance  $dx$  will be equal to  $\alpha ndx$ , where  $n$  is the total number of negative ions present per unit volume at the point considered. Hence the rate at which negative ions are increasing as the positive electrode is approached is given by

$$\frac{dn}{dx} = \alpha n.$$

Thus the number reaching the positive electrode, which is equal to the sum of all the ions generated, is given by

$$\log n/n_0 = \alpha x \text{ (on integrating),}$$

$$\therefore n = n_0 e^{\alpha x} \quad . \quad . \quad . \quad . \quad (24)$$

In other words for every  $n_0$  ions produced in a plane at a distance  $x$  cm. from the positive electrode a number  $n_0 e^{\alpha x}$  reach the positive electrode, assuming that there is no recombination.

If the ionization is confined to a single plane at a definite distance  $a$  from the positive electrode this expression will give the current across the gas. This is the arrangement generally adopted in experiments. If, however, the gas is uniformly ionized throughout its volume, the number of ions formed per c.c. per sec. being  $n_0$  as before, we may proceed as follows. Consider two planes distant  $x$  and  $x + dx$  from the positive electrode, the number of ions formed in this layer will be  $n_0 dx$  and the number reaching the positive electrode due to this layer  $n_0 e^{\alpha x} dx$ . The total number reaching the positive electrode will thus be the integral of this from  $x = 0$  to  $x = d$ ,

$$\text{or} \quad \int_0^d n_0 e^{\alpha x} dx = n_0 \frac{e^{\alpha d} - 1}{\alpha},$$

where  $d$  is the distance between the two electrodes. If there were no ionization by collision the number reaching the electrode in the same time would be  $n_0 d$  which is the number formed by the ionizing agent in the same time. Hence, since the currents are proportional to the number of ions, the actual current  $i$  across the gas is given by

$$i = i_0 \frac{e^{\alpha d} - 1}{\alpha d}, \quad (25)$$

where  $i_0$  is the saturation current.

Similarly equation (24) can be written in the form

$$i = i_0 e^{\alpha x}.$$

**29 Townsend's experiments** Determinations of  $\alpha$  have been made by Professor Townsend (1), to whom the above analysis is due, using a form of apparatus shewn in Fig. 24. He found it more accurate to adopt the arrangement in which the ionization is confined to a definite plane, in this case the surface of the negative electrode. This can easily be effected by using ultra-violet light as the ionizing agent. We shall see (Chapter IX) that ultra-violet light such as is given out by a quartz mercury arc lamp is unable to ionize a gas, but produces a copious

emission of electrons when allowed to fall on a metal plate. These form negative ions on entering the gas by attaching themselves to the uncharged molecules, so that the negative ions may all be regarded as starting from the illuminated plate. It will be noted that in this case there will only be a current through the gas if the illuminated plate is negatively charged.

The ultra-violet light passes into the apparatus through a quartz window *W* and through the lower electrode *P* which consists of a quartz plate silvered on its upper surface. The

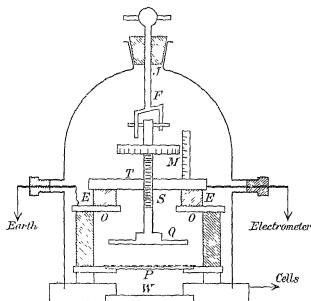


Fig. 24

silvering which is of course opaque is removed in a series of fine parallel scratches over the central part of the plate. The light passing through these scratches falls on the upper electrode *Q*, which is of zinc, since this metal gives a very large emission of electrons under the action of ultra-violet light. The plate *Q* can be moved parallel to itself by means of a thick screw *S* working in a thick brass plate *T*, which is connected to the electrometer by a wire *e*. A micrometer head and scale *M*



allows the position of the plate to be read accurately. The plate  $P$  is in metallic connection with the metal base of the instrument and is charged to a suitable voltage by means of a battery of cells. In order to ensure that no charge should reach  $Q$  except through the gas, a metal ring  $O$  divides the blocks of ebonite  $E, E'$  separating  $P$  from  $T$ , and is put to earth. The screw  $S$  can be rotated (and the distance between the electrodes thus varied) by means of the fork  $F$  which engages two projections on the head of the screw. When readings are to be made the fork  $F$  can be turned so as not to touch the screw and thus perfect insulation is ensured. The fork  $F$  is operated from outside the apparatus by means of an air-tight ground glass joint,  $J$ .

In this apparatus the ions are all formed at the surface of the plate  $Q$  and hence the total current through the apparatus, if the intensity of the illumination remains constant, should be given by the equation

$$i = i_0 e^{\alpha x}$$

where  $i_0$  is the current before ionization by collision sets in, and  $x$  is the distance between the plates. Since the value of  $\alpha$  depends on the *field*, and not directly upon the potential difference between the plates, the voltage must be adjusted for each reading so that the field, which is equal to  $V/i$ , remains constant for the experiment. On making the experiments it was found that the relation (21) was accurately true for a very considerable range of fields.

The value of  $\alpha$  could be deduced by making experiments at two different distances. In this case we have from (24)

$$\frac{i_2}{i_1} = e^{\alpha(r-r_1)}$$

in which  $r_2 - r_1$  is the distance through which the plate  $Q$  has been raised and is read off directly on the micrometer scale  $M$ .

As the ions do not reach their average velocity under the field until they have passed through a thickness of gas comparable with the mean free path in the gas, the equation will obviously no longer apply if the distance between the electrodes is comparable with the mean free path of the ions

in the gas. Hence the apparatus must not be used with too small a distance between the electrodes or, since the m.f.p.  $\propto 1/\text{pressure}$ , with too small pressures of the gas. The pressure can be read off on a gauge attached to the apparatus. Within these limits, and if the experiments are confined to the range of pressures and fields for which the effect of the positive ions in causing ionization is negligible, the results obtained are found to agree very closely with the theoretical curve.

**30 Variation of  $\alpha$  with pressure and field.** The question as to whether a given collision will produce ionization depends, as we have seen, on the energy with which the ion strikes the molecule. The velocity of approach is given by  $X \frac{e}{m} \frac{\lambda}{V}$ . But  $\lambda$  is inversely proportional to the pressure  $p$  of the gas, so that if  $X$  and  $p$  are both increased or decreased in the same ratio the velocity and consequently the energy of impact will be unaltered, and the proportion of collisions which result in ionization will remain the same. On the other hand, the total number of collisions is directly proportional to the pressure, and thus increases as  $p$  is increased. Thus  $\alpha$  is directly proportional to  $p$ , and also to some function of  $\frac{X}{p}$ . These results are expressed mathematically in the form

$$\frac{\alpha}{p} = f\left(\frac{X}{p}\right), \quad (26)$$

where  $f\left(\frac{X}{p}\right)$  represents some undetermined function which remains constant so long as the ratio  $\frac{X}{p}$  is constant. Thus if a curve is plotted between  $\frac{\alpha}{p}$  and  $\frac{X}{p}$  the results should lie on a smooth curve. Professor Townsend (2), experimenting with various gases under many conditions, found this to be the case.

If we apply the results of the kinetic theory of gases to our assumptions we can calculate the form of the function of  $X/p$  which occurs in our equations. The probability that a particle will have a free path greater than some value  $x$

is given by  $e^{-\frac{x}{\lambda}}$  where  $\lambda$  is the mean free path of the particle in the gas. If  $Y$  is the total number of collisions made by a particle in passing through unit distance of the gas the total number of collisions terminating free paths greater than  $x$  will be  $Y e^{-\frac{x}{\lambda}}$ . But since the mean free path is  $\lambda$  we have  $Y\lambda$  equal to 1. Hence the number of collisions in a cm. of gas terminating free paths greater than  $x$  is equal to  $\frac{1}{\lambda} e^{-\frac{x}{\lambda}}$ . The velocity of the ion on striking the molecule at the end of a free path  $x$  is proportional to  $Xx$  where  $X$  is the field, assuming that the velocity is due entirely to the field. If we assume that ionization will occur if this velocity exceeds some constant value  $V$  the coefficient  $\alpha$  will be equal to the number of free paths that exceed the critical value  $x$  given by  $Xx = V$ , or  $x = V/X$ . Substituting this value for  $x$  in the equation and remembering that  $\lambda$  is inversely proportional to  $p$ , we have

$$\alpha = Cp e^{-\frac{CVp}{X}} \quad . \quad . \quad . \quad (27)$$

which gives us the required expression

For a given field the value of  $\alpha$  reaches a maximum for some particular pressure, obtained by differentiating this equation with respect to  $p$ , and equating to zero. In this way we have

$$p_{\max} = \frac{X}{VC} \quad . \quad . \quad . \quad . \quad (28)$$

The experimental results obtained by Townsend are found to agree closely with these equations

The value of  $\alpha$  thus depends on the pressure and the field, it also depends on the nature of the gas. It may be mentioned, as giving some idea of the order of the effect, that in air at a pressure of 4.1 mm. and with a field of 200 volts per cm. the value obtained by Townsend for  $\alpha$  was .50. With the same pressure, but with a field of 320 volts per cm.  $\alpha$  was 2.1, that is to say each ion produced rather more than two fresh ions along each cm. of its track through the gas. The number may, however, be much greater than this. Thus in carbon dioxide at a pressure of 3.95 mm. and with a field of 972 volts

per cm., the number of fresh ions produced along each cm. of the track was no less than 4330.

Although the most accurate results are obtained by ultra-violet light, the apparatus can be modified to allow the use of other ionizing agents. It is found that the results are the same whether the ionization is due to the action of, say, X-rays on the gas itself or to the liberation of electrons from the metal electrode. Thus the nature of the ions depends only on the gas and its pressure and is independent of the nature of the ionizing agent.

**31. Minimum velocity required to produce ionization.** The method of ionization by collision enables us to obtain a

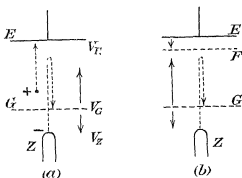


Fig. 25

value for the minimum velocity required to produce an ion in a gas. The simplest arrangement is that indicated in Fig. 25 (a). The electrons are usually supplied by an incandescent filament  $Z$ , electrically heated, while parallel to this at some little distance from it are a piece of wire gauze  $G$  and a metal plate  $E$ , the latter being connected to an electrometer. The plate  $E$  is at zero potential, while  $G$  and  $Z$  are both maintained at a positive potential the potential of  $G$  being greater than that of  $Z$ . The electric fields are thus directed in each case away from the gauze. Consider now an electron liberated from the filament  $Z$ . It is acted upon by the field and reaches  $G$  with a velocity  $v$ , given by  $Ve = \frac{1}{2}mv^2$ ,  $v^2 = \frac{2Ve}{m}$  where  $V$  is the potential difference between the two plates. If this velocity

is sufficient to produce ionization by collision with the molecules of the gas, positive ions will be formed in the space between  $G$  and  $E$  and will find their way under the action of the field to the electrode  $E$ , and there will thus be a current through the gas which will be recorded by the electrometer. If no collisions result in ionization the negative ion on entering the space between  $G$  and  $E$  finds itself in an adverse field and since  $V_G - V_E$  is greater than  $V_G - V_Z$  the velocity of the ion will be reversed before reaching  $E$  and it will return to the electrode  $G$  or  $Z$ . Thus the minimum difference of potential between  $Z$  and  $G$  for which a current is registered in the electrometer gives the minimum potential energy required to ionize the molecules of the gas between the electrodes.

Recent experiments (3) made on this principle have shown that the minimum value of  $V_G - V_Z$  necessary to produce ionization is for hydrogen 16.9 volts, for oxygen 15.5 volts, for helium 25.2 volts and for nitrogen 16.9 volts. Since  $e$  has the value  $4.77 \times 10^{-10}$  e.s.u. and 1 volt is  $1/300$  e.s.u. this corresponds to an amount of energy in the particles of  $2.68 \times 10^{-12}$  ergs in the case of hydrogen,  $2.47 \times 10^{-12}$  ergs for oxygen with corresponding values for the other gases. As the pressure is so low that we may assume that the negative particle is an electron the ratio  $e/m = 1.77 \times 10^7$  e.m.u. per g.m., and  $V = 16.9 \times 10^8$  e.m.u. Substituting in the equation we find that the velocity which the particle must have to produce ionization in hydrogen is  $2.15 \times 10^8$  cm. per sec.

We have so far assumed that the ion is moving only under the action of the applied field. Owing to the fact that it is in a gas it will share the ordinary thermal agitations of the molecules of the gas and will thus have a velocity independent of that produced by the field. It can be shown that for an electron at ordinary temperatures this velocity of thermal agitation would amount to about  $10^7$  cm. per sec. This is only one-twentieth of the ionizing velocity and hence can be neglected without introducing any serious error into our calculations.

**32 Resonance Potentials.** When experiments are conducted by the method outlined in § 31 the electrode  $E$  begins to acquire a positive charge when the accelerating potential applied to the

electrons is considerably below the values given at the end of that section, and for a considerable time these lower values were thought to be the ionization potentials for the different gases employed. More careful investigation has shewn that this is not the case and that there is no ionization in the gas itself at these lower values. This can be proved very simply by inserting a second gauze sheet between  $G$  and  $E$  and parallel to both (Fig. 25 (*b*)). As in the earlier experiments the electrons from  $Z$  are accelerated by the field between  $Z$  and  $G$ , and retarded by the field between  $G$  and  $F$ , the potential difference between  $F$  and  $G$  being slightly greater than that between  $G$  and  $Z$ . Thus no negative electrons can reach the gauze  $F$ . The positive ions formed, however, are attracted towards  $F$  and pass through it. Here however they meet a retarding field, and if the potential difference between  $E$  and  $F$  is greater than that between  $G$  and  $F$  no positive ions from the space between  $F$  and  $G$  will be able to reach the electrode  $E$ . With this disposition of fields no ions from the space  $FG$  can reach the electrode.

When, however, the experiment is performed, say in helium at low pressure, the electrode begins to charge up when the accelerating field is 20.4 volts, the value originally taken as the ionization potential for helium. This, as we have seen, cannot be due to ionization of the gas by the electrons. As a matter of fact, it has been proved to be due to ultra-violet radiation excited in the molecules of the gas by the impact of the electrons upon them. This radiation produces an emission of electrons when it falls upon a metal surface (see § 73), and it is this photo-emission which causes the charging up of the electrode. If the stream of electrons is sufficiently intense the radiation can, in many cases, be detected spectroscopically, and is found to consist of a single line out of the whole spectrum of the gas concerned. This was first observed by Frank and Hertz in mercury vapour, but the observations have since been extended to many other metallic vapours. The minimum potential difference through which the electrons must have fallen to excite this radiation in the gas is called the resonance potential for the gas. Thus the resonance potential for helium is 20.1 volts.

If, however, the accelerating potential,  $V_G - V_Z$ , is increased

ionization of the gas is eventually produced. The value of the accelerating potential difference which will just enable the electrons to produce ions in the gas by their direct action is the true ionization potential for the gas. In the case of helium it is 25.7 volts. The existence of ionization can be detected by reversing the sign of the field between  $E$  and  $F$ . Ions are then drawn to  $E$  from the gas, and the setting in of direct ionization is marked by a sudden increase in the rate at which the electrode  $E$  charges up. It may be mentioned that as soon as ionization sets in the gas emits its complete optical spectrum. We shall have occasion to refer to this subject again in a later chapter.

The ionization potential measures the energy required to remove an electron completely from its parent atom. The resonance potential must measure the energy required to transform the atom into some abnormal condition, most probably by transferring one of the atomic electrons from its normal position in the atom to some other position within the atom in which it possesses a greater energy. If the energy of the incident electron is less than this value, it is apparently unable to transfer any portion of its energy to the atom, and the collisions are then perfectly elastic.

**33 Ionization by collisions with the positive ions.** We have seen that if the field is less than a certain value ionization is produced only by the negative ions in the gas. It is found, however, experimentally, that when the field is large the current increases more rapidly than would be the case if the negative ions alone were acting. For these fields we must assume that the positive ions also produce fresh ions by colliding with the molecules of the surrounding gas.

We can easily calculate the form of the expression for the current if we assume that a positive ion forms  $\beta$  fresh ions for each cm. of its path through the gas. The simplest case is that where the initial ionization is all produced at the negative electrode, for example, by the action of ultra-violet light. This corresponds to the experimental arrangements of Fig. 21.

Consider a pair of planes  $AB$  and  $CD$  parallel to the electrodes at a distance  $dx$  apart and  $x$  cm. from the negative electrode

Let  $p$  be the number of pairs of ions generated by both positive and negative ions between the negative electrode and  $AB$ , and  $q$  the number of pairs of ions generated between  $CD$  and the positive electrode. The number of ions arriving at the positive electrode per second is thus  $n = p + q + n_0$  where  $n_0$  is the number generated per second at the negative electrode. The number of pairs of ions generated between  $x$  and  $x + dx$  is

$$(n_0 + p) \alpha dx + q \beta dx \quad . \quad . \quad . \quad (29)$$

since all the negative ions generated per second cross the planes in one direction and all the positive ions in the space below the planes cross them in the opposite direction, assuming that there is no recombination. This is obviously true since the saturation voltage is exceeded before ionization by collision begins. Substituting for  $q$  we have

$$\frac{dp}{dx} = (n_0 + p)(\alpha - \beta) + n\beta.$$

The solution of this equation is of the form

$$n_0 + p = A e^{-(\alpha - \beta)x} - \frac{n\beta}{\alpha - \beta}$$

and  $A$  can be found from the condition that  $p = 0$  when  $x = 0$ . Thus substituting for  $A$  and solving for  $n$  we have

$$n = n_0 \frac{(\alpha - \beta) e^{(\alpha - \beta)d}}{\alpha - \beta e^{(\alpha - \beta)d}}, \quad . \quad . \quad . \quad (30)$$

where  $d$  is the distance between the electrodes

This equation is due to Townsend and was carefully tested by him with the apparatus already described.<sup>(1)</sup> It was found that an expression of this form represented the experimental results with considerable accuracy over the whole range of distances and forces.

The values of  $\beta$  are generally small compared with those of  $\alpha$  and equation (30) shews that under these circumstances the effect of ionization by the positive particles will only be appreciable for large values of the field or for large values of  $d$ . The value of  $\beta$  deduced from the equation is relatively greatest in the case of hydrogen and decreases with increasing atomic weight of the gas. Thus for hydrogen in a certain experiment



$\beta$  was about one-fortieth of  $\alpha$ , or the proportion of ions formed by collision of the positive particles per cm. was only one-fortieth of that formed by the negative. For air the ratio of  $\beta/\alpha$  was less than one per cent. and for carbon dioxide less than 1/1000.

The positive ions are molecules of the gas, while the negative as we have seen are at the pressures used in these experiments probably electrons. Thus we see that for a given amount of energy the efficiency of a particle as an ionizing agent decreases rapidly as the size of the particle is increased.

**34. The spark discharge.** The equation (30) just developed suggests curious possibilities. It is evident that the current will become infinite for some distance  $d$  such that

$$\alpha = \beta e^{(\alpha - \beta)d}. \quad (31)$$

This case corresponds to what is known as the spark discharge. A considerable amount of experimental research has been devoted to the spark discharge. If two electrodes are separated by a gas at any pressure and the difference of potential between them is gradually increased eventually a point is reached at which a bright spark accompanied by the well-known crackling noise will pass between them and the two conductors become completely discharged. If the difference of potential is continuously restored by connecting the two electrodes to an electrical machine a continuous torrent of sparks is obtained which may pass into the form of an arc. In this case the current may rise to many amperes.

The spark may also be made to pass by bringing the electrodes nearer together as in the case of the discharge of a Leyden jar by discharging tongs, or by reducing the pressure of the gas between the electrodes. This latter is, however, only effective down to a certain point. It is found that for any given distance apart of the electrodes there is a critical pressure at which the discharge passes most easily. Reducing the pressure below this critical value causes a very rapid rise in the potential necessary to produce a spark, so that the potential at very low pressures may easily exceed by many times that which would suffice to

produce discharge at the same distance in an at atmospheric pressure

The critical potential difference between the electrodes necessary to produce a spark is called the sparking potential. If we assume that the spark takes place between two parallel plate electrodes situated  $S$  cm apart the value of the sparking potential is equal to  $XS$  where  $X$  is the field between the plates.

Thus if  $\alpha$  and  $\beta$  are the two coefficients of ionization under the conditions of the experiment, sparks should pass between the electrodes when their distance apart is given by

$$\alpha = \beta e^{(\alpha - \beta)S} \quad (32)$$

and the sparking potential should be equal to  $XS$  where  $X$  is the field between the plates

This equation was tested by Townsend  $\alpha$  and  $\beta$  were measured for some definite field  $X$  and the value of  $S$  calculated from equation (32). The plates were then set at this distance apart and the potential difference between them gradually increased until a spark passed. The minimum sparking potential as thus obtained was found to agree in every case with the product  $XS$  as previously determined, the divergence between the two values being less than one per cent. This agreement is strong proof of the substantial accuracy of the theory

It will be seen that this theory requires the existence of a certain number of free ions in the gas between the electrodes if the spark is to pass. Under normal circumstances the air generally contains a few ions especially if the electrodes are illuminated by sunlight which contains a small proportion of ultra-violet light. If, however, the ions present are very few, as, for example, if the sparking experiments are made in the dark, a considerable time may elapse before the small number of ions originally present have increased sufficiently in number to give rise to a spark discharge, and under these circumstances the difference of potential may be increased considerably beyond the critical sparking potential without a spark passing. This phenomenon is well known and is called the retardation of the spark. Under certain circumstances this retardation may amount to several minutes. It is reduced to zero if the negative

electrode is exposed to a weak source of ultra-violet light. Many early experiments were vitiated by the neglect of this precaution

**35 Sparking potential for parallel plate electrodes** The conditions are most easily interpreted when the electrodes take the form of a pair of parallel plates. Experiments of this kind have been made by Carr (5), using apparatus as shewn in Fig. 26. If the discharge is taken between two metallic plates in the usual way it is found that the spark always passes between rough points or small projections on the edges of the disks. To avoid this the electrodes  $E, E$  were completely embedded

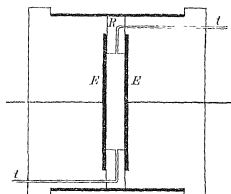


Fig. 26

in ebonite except for a portion near the centre which was carefully planed and polished. The plates were separated by ebonite rings  $R$  of varying thickness so that spark lengths of different values could be used. The gas to be experimented on could be introduced by fine tubes  $t, t$  running through the ebonite, and the whole apparatus was made air-tight.

The experiments shewed that for a given gas there was a minimum potential difference depending only on the nature of the gas below which a spark would not pass. For any given distance between the plates it was always possible to find some pressure at which the spark passed at this minimum potential. Either increasing or decreasing the pressure from

this critical value increased the sparking potential. These results are shown in Fig. 27 which represents some of Carr's observations on air at various pressures and for various distances between the electrodes. Similar results were obtained for other gases. The minimum sparking potential for hydrogen is about 280 volts, the critical pressure being 10.3 mm., when the sparking distance is 1 mm. and 1.46 mm. with a sparking distance of 10 mm. For air the minimum potential is about 340 volts and for carbon dioxide 419 volts. Within the limits of experimental error the product of the sparking distance into the critical pressure is a constant for a given gas. For different gases this

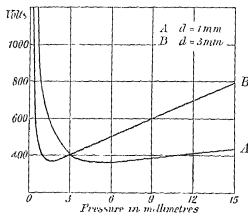


Fig. 27

product is approximately proportional to the mean free path of the molecules of the gas.

**36. Paschen's Law.** As the result of a large number of experiments Paschen (6) came to the conclusion that the sparking potential was a function only of the product of the sparking distance into the pressure of the gas, that is to say, of the mass of gas between unit area of the electrodes. This result applies also to the case of the discharge between two spheres if the distance between the spheres is appreciably less than the radius of curvature. It can easily be shown that this result follows from the theory given above. Let  $V$  be the sparking potential.

Then  $V = SX$ , and if  $M$  represents the product  $\mu S$  we have from (26)

$$\alpha = pf \left( \frac{X}{p} \right) = \frac{M}{S} f \left( \frac{V}{M} \right),$$

$$\beta = p\phi \left( \frac{X}{p} \right) = \frac{M}{S} \phi \left( \frac{V}{M} \right).$$

Hence, substituting in the equation (32),

$$\alpha = \beta c^{(\alpha - \beta)S}$$

we have

$$(\alpha - \beta)S = \log_e \left( \frac{\alpha}{\beta} \right),$$

$$\therefore M \left[ f \left( \frac{V}{M} \right) - \phi \left( \frac{V}{M} \right) \right] = \log \left[ f \left( \frac{V}{M} \right) / \phi \left( \frac{V}{M} \right) \right], \quad (33)$$

thus shewing that the sparking potential  $V$  depends only on  $M$ , that is, the product  $\mu S$ . Carr has shewn that this law is true for all pressures both above and below the critical pressure. It is thus a result of great importance. It follows that if  $p$  and  $S$  are varied in such a way that the product  $\mu S$  remains constant the sparking potential will be unaltered. Hence in order to be able to calculate the sparking potential for any given distance apart of the electrodes, and for any pressure of the gas, it is only necessary to have a complete set of observations on the variation of sparking potential with pressure for one definite spark length. For example to find the value of the sparking potential for a sparking distance of 10 cm in air at 10 mm. pressure, in which case the product  $\mu S$  is 100, reference to a standard curve for air shews that this product corresponds to a sparking potential of 5000 volts.

At pressures considerably above the critical pressure the relation between  $V$  and  $\mu S$  is practically linear and we can write

$$V = A + B(\mu S) \quad . \quad . \quad (34)$$

For air the values of  $A$  and  $B$  are respectively 1700 and 39, for hydrogen 1860 and 25.6

**37 Variation of sparking potential with temperature**  
Paschen's law applies also to different temperatures at any rate up to 300° C. Thus if the experiment is arranged so that

the mass of gas between the electrodes remains constant (i.e. if the vessel is air-tight) increasing the temperature produces no alteration in the spark gap. If the gas is allowed to expand the sparking potential is that associated with the new density of the gas.

**38 The brush discharge.** If the conductors are of small dimensions and are separated by considerable distances so that the field between the electrodes is far from uniform the discharge presents a different appearance. Instead of one or more bright sparks passing completely from one electrode to the other a luminous brush is formed at the part of the conductor where the field is most intense fading away as the distance from the electrode increases. If the brush is examined minutely it is seen to consist of a large number of small sparks commencing at the electrode and terminating in the air. The luminous discharge is thus not continuous between the electrodes. If, however, the pressure of the gas is reduced the luminosity may grow until it reaches completely from one electrode to the other, in which case it is frequently stunted.

The minimum potential required to start a brush discharge from a point depends on the sign of the point; the requisite potential being greater for a positive point than for a negative. The conditions for a discharge are obviously that the positive ions shall be able to acquire sufficient energy to produce an adequate supply of negative electrons to carry the current. Now if the point is negative the positive ions are moving towards it and may produce electrons (1) by collision with the molecules of the gas, as in the cases already considered, and (2) by collision with the metal of the electrode. If the point is positively charged only the first of these sources is available and hence we might expect that the discharge would pass more readily from a negative than from a positively charged point.

Let us suppose now that the point is equivalent to a small sphere of radius  $a$ . If the potential of the sphere is raised to  $V$  the difference in potential between the sphere and a point distant  $x$  from its surface is given by  $Vx/(a+x)$ . Suppose  $\alpha$ , Fig. 28, is the curve connecting sparking potential with

distance for the given pressure of the experiment. If the difference of potential is so large that the curve  $\beta$  relating difference of potential and distance cuts the sparking curve, a discharge will take place from the point to the air. The smallest value of the potential of the point for which the discharge takes place will be when the curves just touch as shewn in the figure. It can easily be seen from the character of the curves that they must touch at some point not far distant from the minimum sparking potential. Hence approximately

$$V \frac{x_0}{a + x_0} = V_0,$$

$$V = \left(1 + \frac{a}{x_0}\right) V_0 \quad . \quad . \quad (35)$$

where  $V_0$  is the minimum spark potential, and  $x_0$  the corresponding distance

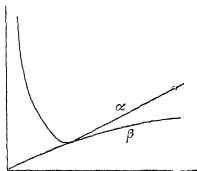


Fig 28

**39. The dark discharge** Although we have considered the conditions that a discharge may take place, it by no means follows that the discharge will be a luminous one. The discharge between a point and a plane frequently commences, and can be measured by a galvanometer, before any sign of luminosity is to be seen. If the potential of the point is increased a glow forms on the point and subsequently a brush discharge may be formed. If the current is increased sparking takes place, which with further increase in current may produce an arc. At this stage the ratio of the current to the potential

difference is very largely increased. In the case of the arc discharge the electrons carrying the current come mainly from the electrodes which usually become intensely hot. The conditions are, therefore, somewhat different to those of the spark, where the ions are formed from the molecules of the gas, and we shall not consider it further at this point. These results

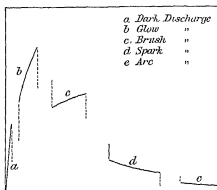


Fig. 29

are shewn graphically by the curves in Fig. 29, in which the ordinates represent potentials and the abscissae the corresponding values of the current.

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## CHAPTER VI

### THE PHENOMENA OF THE DISCHARGE TUBE

40 Phenomena of the discharge in a gas at low pressure. If the discharge takes place between electrodes enclosed in a glass tube containing gas at low pressure, say, from a millimetre or so downwards, some very beautiful and interesting effects are observed. If the potential difference across the tube is not much more than the minimum necessary to maintain a current through the tube the luminosity is at first confined to the region of the two electrodes, the rest of the discharge being dark, as indicated in Fig 30. As the

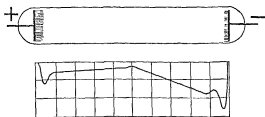


Fig 30

pressure of the gas is reduced, say, to about one mm. or so of mercury, the two glows extend outward especially that at the positive electrode which now occupies the major portion of the tube. The potential necessary to maintain a current across the tube has now its minimum value.

As the pressure is still further reduced it is seen that the glow near the cathode consists of two parts separated by a dark space. The glow nearest the cathode, covering its surface with a velvety light, is called the *cathode glow*, the other which is much more extensive stretching at low pressures some considerable distance into the tube is known as the *negative glow*. The space between them which is comparatively non-

luminous is the *Crookes dark space*, while the similar region between the negative glow and the positive column is known as the *Faraday dark space*. At pressures of a millimetre or so of mercury the positive column presents a uniform luminosity, but as the pressure is reduced it generally breaks up into a series of bright and dark striae. The typical appearance of a

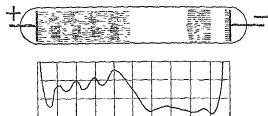


Fig. 31

discharge tube at this stage is represented in Fig 31, which corresponds to a pressure of about half a mm. in the case of an.

The length of the tube occupied by the phenomena near the negative electrode depends principally upon the nature and pressure of the gas and is independent of the length of the discharge tube. The rest of the tube, however long, is filled by the positive column.

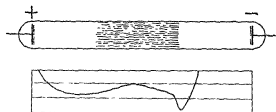


Fig 32

As the pressure is reduced still further the negative glow and the Crookes dark space increase in length while the positive column contracts towards the anode and at very low pressures is represented only by a feeble glow on the surface of the anode (Fig. 32). at this stage there is no region of constant intensity in the tube. Finally if the exhaustion is pushed to extreme

limits as in a X-ray bulb, the Crookes dark space expands until it fills the whole of the discharge tube which is then entirely dark. At this stage the walls of the glass vessel fluoresce brightly, the fluorescence being bluish with soda glass, and greenish with German glass. The greenish coloration is probably due to traces of manganese.

41 Investigation of the intensity of the field in various parts of the discharge. The electric intensity in various parts of the discharge has been investigated by many observers. The most usual way is to insert in the tube a small subsidiary electrode consisting of a fine pointed platinum wire. If there are free ions in the tube and the potential of the wire is less than the potential of the space in its immediate neighborhood there will be a field in the gas tending to drive ions of the appropriate sign up to the wire. For example if the wire has a smaller potential than the surrounding gas the field will drive up positive ions until the potential of the electrode becomes equal to that of the gas.

The accuracy of the method obviously depends on there being a plentiful supply of ions of both signs in the gas around the wire. If ions of one sign only are present the results may be very misleading. For example supposing only negative ions are present which is practically the case at points in close proximity to the anode, these negative ions will strike the surface of the wire and continue to do so until its negative potential is so high as to prevent by its electric repulsion any further ions from reaching it. As there are no positive ions to neutralize it, it will thus acquire a negative potential which may be considerably higher than that in any part of the original space before the introduction of the wire. Hence at points very near either electrode the results obtained by the exploring wire are apt to be misleading. In the main part of the discharge its results are no doubt sufficiently near the truth.

The method has been applied by means of the apparatus shown in Fig. 33. The electrodes *C* and *A* were kept at a fixed distance apart by means of the glass rod *d* to which they were both attached. The glass tube containing the electrodes was

much longer than the distance between the electrodes which were connected to terminals passing through the ends of the tube by long wire spirals. A piece of soft iron  $R$  attached to one electrode enabled the electrodes to be moved about from one end of the tube to the other by means of a magnet. Two electrodes,  $e, f$ , were sealed into the tube, the line joining them being along the axis of the tube, and their distance apart about 1 mm. If the two electrodes are connected to opposite quadrants of an electrometer the deflection indicates the difference of potential between the two points that is, since  $ef$  is constant, it is proportional to the field in the gas in the region of  $e, f$ . By sliding the electrodes along this region could be made to coincide with any part of the discharge, and in this way the field in any part of the discharge could be investigated.

An ingenious method which does not involve the uncertainties of the previous method is due to Sir J. J. Thomson (1). In this

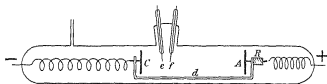


Fig 33

the fact that a beam of cathode rays is deflected by an electric field is made use of. It will be shewn later (§ 47) that the deflection of the rays is proportional to the field through which they pass. The main discharge passes between  $C$  and  $A$  (Fig 34), the experimental devices for moving the discharge electrodes being the same as in the apparatus just described. The cathode rays are generated in a side tube  $T$  at right angles to the discharge, and pass across the main discharge through a fine hole in the metal ring  $G$  which serves as anode. The deflected beam passes down a long tube  $S$  falling on a screen at the end of the tube where the deflection of the beam is readily measured. This method has been applied to investigate the field very near the cathode.

The results obtained vary somewhat with the state of the discharge, and are shewn in Figs. 30-32 immediately below the

diagrams of the discharge to which they refer. It will be seen however that they present certain constant features

Starting at the cathode there is a very strong field in the Crookes dark space which drops with considerable rapidity as we approach the negative boundary of the negative glow where indeed it reaches its minimum value for the tube. Since the field is very strong the fall of potential between the surface of the cathode and the edge of the negative glow is very considerable and in many cases accounts for the greater part of the whole fall of potential across the tube. This is known as the *cathode fall of potential*. The field in general rises again slightly

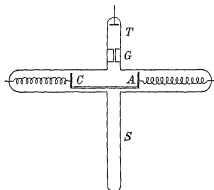


Fig 34

in the negative glow and falls again in the Faraday space rising gradually as the edge of the positive column is approached

If the positive column is uniform or unstriated the field has a constant value until the neighbourhood of the anode is reached when there is again a sharp increase in the field accompanied by rapid increase of potential up to the anode. This anode fall of potential is, however, always much less than that at the cathode.

If the column is striated the field shews variations superimposed upon the steady field, the field being a maximum where the striation reaches its maximum brightness. This is shewn in Fig 31.

**42 Number of ions in various parts of the discharge.**  
The apparatus of Fig 33 can be modified so as to give the

relative number of ions in different parts of the discharge. If the two points *e, f* are replaced by two small plates, their planes being parallel to the discharge, the current between the plates when some small constant difference of potential is maintained between them (say, for example, that of a Clark cell), will by (5), § 13, be roughly proportional to the sum of the ions of each kind present in the gas at the given point. In this way by moving the discharge so that various parts of it come between the plates the distribution of ions in the discharge can be found. The results obtained by H. A. Wilson (2) are shewn in Fig 35. It will be noticed that the number of ions is very small near the anode and again in the Crookes

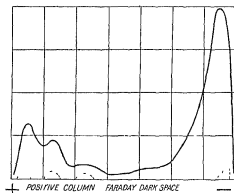


Fig 35

dark space. It rises to a maximum in the negative glow, falls again in the Faraday dark space to rise again in the positive column. If the column is situated the ions are most numerous in the luminous parts and less numerous in the dark parts.

Recently, however, van der Pol (3) has investigated the matter by a method not involving the use of subsidiary electrodes, with their attendant uncertainties. The discharge tube is placed between the plates of a small parallel plate condenser which forms part of an oscillating circuit, the current in which can be measured by a Duddell galvanometer. If the medium between the plates becomes slightly conducting the current in the circuit diminishes as the conductivity increases. By bringing different parts of the

discharge tube successively between the condenser plates the relative conductivities of the different portions of the discharge can be estimated. It was found that if the positive column was unstriated the conductivity along it was constant and somewhat higher than that in the dark space. If the column was striated the conductivity was found to be a minimum at the bright edge of the striation. This is exactly the reverse of Wilson's result. It is, however, what might be expected from Sir J. J. Thomson's observation that the field is a maximum at this point. A large field would tend to remove the ions from the space more rapidly than a small field, and the ionization and hence the conductivity should be smaller as found by van der Pol.

**43 The cathode fall of potential.** The fall of potential which occurs in the neighbourhood of the cathode is often a very large fraction of the whole fall of potential across the tube. If the current density of the discharge is not too large the cathode fall depends only on the nature of the gas and of the electrode and is independent of the potential difference between the electrodes. If the current density is low the cathode glow only occupies part of the cathode, the area covered increasing as the current is increased. As long as the cathode is not completely covered the cathode fall remains constant, after this stage is passed, if the current through the tube is still further increased, the cathode fall increases with the current.

The fall of potential varies with the nature of the gas. For platinum electrodes it is about 340 volts in air, 300 volts in pure hydrogen, 167 volts in argon, and 470 volts in water vapour. The value is very nearly the same for electrodes of any of the less electropositive metals such as platinum, silver, copper, or iron, but is considerably reduced in the case of the active metals such as magnesium, sodium, or potassium. In the latter case the normal fall is no more than 172 volts in hydrogen, and 69 volts in argon, which is the smallest value yet recorded. This is probably due to the ease with which these metals emit negative electrons.

The anode fall of potential is much less than that at the cathode and varies little either with the pressure or nature of

the gas, or the nature of the electrodes. It lies between 18 and 24 volts.

**44. Theory of the discharge.** The theory of ionization by collision can be extended to include the phenomena of the discharge tube. Let us suppose that the discharge is passing through the tube and that conditions have become steady. The ions necessary to carry the current from one electrode to the other are supplied by the collision of the ions already present with the molecules of the residual gas. It is evident that, in the absence of an external agent, a continuous supply of ions can only be obtained if both positive and negative ions produce fresh ionization in this way. Consider first the positive ions in the gas. The field near the negative electrode is many times greater than the field at any other part of the discharge. Hence the positive ions will attain their maximum velocity in the neighbourhood of the cathode. It is uncertain whether the negative ions are produced by the impact of the positive particles on the metal of the cathode itself or on the molecules of gas near it. In any case since the field increases so rapidly near the cathode the bulk of the ionization will occur in a layer of the gas so near the cathode that the negative ions may be regarded as starting from the cathode itself. As the cathode field is so great the negative particles formed will be removed with considerable velocities by the field and hence there will be very few negative ions in the immediate neighbourhood of the cathode. This has been proved experimentally by Sir J. J. Thomson. There will thus be a considerable accumulation of positive ions just in front of the cathode. This accumulation of positive electricity near a negatively charged surface explains the very large values of the field in this region.

The negative particles, which at these pressures are all electronic, will move away from the cathode with high velocities and will produce ions by collision with the molecules of the residual gas. If we associate luminosity with ionization the gas will become luminous when ionization commences and this point will mark the beginning of the negative glow. The Crookes dark space, therefore, represents the distance fallen through



by the negative particles before collision begins, and thus should be comparable with the mean free path of the electrons in the gas. This is found to be approximately the case. The presence of the excess positive charge in the Crookes dark space, however, reduces the value of the electric field in the space beyond it. Hence the field in the negative glow falls rapidly to a value which soon becomes insufficient to give to the electrons the energy necessary to produce fresh ionization, and luminosity ceases. This corresponds to the commencement of the Faraday dark space. The current in the dark space is here carried by negative ions drawn from the negative glow. There is, therefore, an excess of negative electricity in the dark space and this accumulation tends to increase the field between the dark space and the positive electrode. The field thus increases steadily through the dark space and finally attains a sufficiently high value to enable the negative ions again to ionize by collision. Hence luminosity is restored and we have the beginnings of the positive column. As the field in the positive column remains practically uniform, ionization by collision of the negative ions will occur along its whole length and we shall get a uniform column of light. If, however, there happens to be an accumulation of positive ions at any point, this may produce a local fall of field and the discharge will cease to be luminous at that point. Just as in the case of the Faraday dark space this loss of ionizing power will be attended with an accumulation of negative electricity which will restore the field to its normal value. Thus a series of striae may be set up in the positive column, as is often found to be the case. The non-luminous parts of the striae on this hypothesis are thus a repetition of the phenomena of the Faraday dark space.

To sum up, luminosity occurs when the ions have sufficient velocity to produce fresh ions by collision, in the dark portions of the discharge the current is carried by ions drawn from the luminous parts of the tube.

It will be seen that on this hypothesis the phenomena are maintained by the collision of positive ions from the Crookes dark space with the cathode. That this is so may be readily

illustrated by a very simple experiment. Some solid obstacle often in the form of a mica cross is placed in the tube and arranged so that it can be turned when required into the path of the discharge. If the obstacle is placed on the anode side of the Crookes dark space a shadow is cast on the anode owing to the stoppage of the stream of negative particles. If, however, the obstacle is placed within the Crookes dark space, not only is there a shadow cast on the anode but a corresponding shadow appears on the cathode, the glow entirely disappearing from that portion of the cathode which is shielded by the obstacle. Hence the phenomena at the cathode are due to particles approaching it from the boundary of the Crookes dark space. Since they approach a cathode they must be positively charged.

It is not necessary for the maintenance of the discharge that the average field across the tube shall be sufficient to cause the positive particles to ionize. It is sufficient that it shall rise to this value in a short region near the cathode. But the irregularities in the field between the electrodes which give rise to cathode fall of potential are due to the accumulation of positive ions near the cathode. This accumulation is an effect of the discharge and is not initially present. Hence it will require a considerably higher voltage to start the discharge than will be necessary to maintain it when it has once begun. This result has also been verified. If the discharge is started by a small induction coil, a steady voltage of 470 volts is sufficient to maintain the discharge in air at a pressure of one mm of mercury with a distance of 11.5 cm. between the electrodes. With this voltage the current was of the order of one milliampere. The voltage required increases as the pressure is reduced, a potential of about 1000 volts being required if the pressure is reduced to 1/10 mm.

If the pressure is very much reduced so that the tube is practically dark throughout, much higher voltages may be necessary. In the case of the tubes used for X-ray work 100,000 volts are often required to maintain a current of a few milliamperes across the tube, and it is possible to exhaust the tube to such an extremely low pressure that the highest potentials yet available are insufficient to start a discharge through it.

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## CHAPTER VII

### CATHODE RAYS AND POSITIVE RAYS

45 **Cathode rays.** When the pressure in the tube is sufficiently low another phenomenon may be noticed, quite distinct from the glows already described, namely, a beam of bluish light proceeding normally from the cathode along the tube and penetrating to a greater or shorter distance along it as the pressure is comparatively low or high. If the pressure is sufficiently reduced these rays may reach the further boundary of the tube in which case vivid fluorescence is excited on the part of the glass on which they strike. These streamers are known as the *cathode rays*

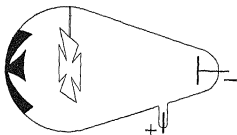


Fig 36

The nature of these streamers was for long a subject of discussion. Goldstein, to whom the name is due, regarded them as some kind of disturbance in the ether. Crookes suggested that they were streams of highly charged particles of some very attenuated form of matter, projected by the electric forces from the surface of the cathode. The latter view is now universally accepted. The evidence for this hypothesis will appear from the following summary of the properties of the rays.

(1) *The rays travel in straight lines.* This can readily be shewn by constructing a discharge tube of the form of Fig 36,

in which some obstacle, generally in the form of a mica cross, is placed in the path of the rays. A shadow of the obstacle appears in the centre of the fluorescence caused by the rays on the further boundary of the tube.

(2) *The rays emerge normally from the cathode.* If a tube such as that just described is constructed with a large plane cathode and a small obstacle such as a wire is placed near it a sharp shadow of the wire appears on the further wall of the tube without any sign of penumbra around it. If the rays were given off in all directions from the cathode (as, for example, light is emitted from a uniformly illuminated disk) no shadow of the wire would be seen. Similarly if the cathode is concave the cathode rays come to a focus at some point along the axis. Owing to the mutual repulsion of the rays the focus is generally somewhat beyond the geometrical centre of the concave surface. This property of the rays is made use of in the construction of X-ray tubes.

(3) *The rays can penetrate small thicknesses of matter* such as sheets of aluminum foil or gold leaf without producing perforations in the metal. This discovery, which was due to Hertz, can be demonstrated by constructing a "window" of thin aluminum leaf in the end of the tube struck by the rays. The passage of the rays through the foil is demonstrated by luminous blue streamers in the air on the far side of the leaf. These are sometimes known as *Lenard rays*.

(4) *The cathode rays are deflected by a magnetic field.* If an ordinary bar magnet is held near a discharge tube the deflection of the rays by the magnet is made evident by the movement of the fluorescent spot which they produce on the further boundary. We shall return to this important point later. The direction of the deflection shews that the cathode rays experience the same deflection as would be experienced by a flexible conductor coinciding with the path of the rays and carrying an electric current, the direction of the current being towards the cathode.

(5) *The rays carry a negative charge.* This was demonstrated by Perrin (1) in 1895. A slight modification of Perrin's original experiment is shewn in Fig. 37.

The cathode *A* is contained in a small side tube which also contains the anode *B*. The rays starting from the cathode pass through a small slit in a brass plate *C* across the larger bulb *D*, where they manifest themselves by phosphorescence of the walls of the bulb. Enclosed in this bulb but out of the direct line of fire of the cathode stream is a small cylindrical vessel *E* having a small aperture facing the centre of the bulb. This vessel is carefully insulated and connected by the electrode *F* to an electrometer. The vessel is screened from the powerful electrostatic disturbances in the discharge tube by surrounding it with a nearly closed metal vessel *G* which is connected to earth. This arrangement forms what is known as a *Faraday cylinder*.

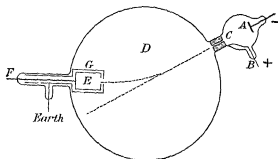


Fig 37

When the discharge was passed the inner cylinder received a very small negative charge. If, however, the cathode rays were deflected by a magnet so as to fall on the openings in the Faraday cylinder a very large negative charge was recorded by the electrometer. This charge increased for some little time but finally became constant owing to the fact that the cathode rays turned the residual gas in the discharge tube into a partial conductor. The charge on the vessel increased until the loss by conduction through the ionized gas (which is roughly proportional to the potential of the Faraday cylinder) was equal to the gain from the cathode stream. This experiment proves conclusively that a negative charge is a necessary accompaniment of the cathode stream.

(6) *The rays are deflected by an electrostatic field* This effect, which was a necessary consequence of the theory that the rays consist of charged particles, was for some time sought for in vain. The results just described gave a clue to the cause of the failure. We have seen that the cathode rays ionize the gas through which they pass, thus making it a partial conductor. In fact they move down the discharge tube through a sort of protecting conducting cylinder of their own construction, and are thus screened from the action of any electric field applied to the tube, there being, of course, no electrostatic field inside a closed conductor. By exhausting the tube very completely of the residual gas Professor Sir J. J. Thomson<sup>(2)</sup> in 1897 succeeded in partially eliminating this effect and demonstrated the direct deflection of the cathode rays by an electrostatic field. The direction of the deflection shewed that the particles in the rays were negatively charged.

(7) In addition to these effects the cathode rays can exert mechanical pressure, and convey very considerable amounts of kinetic energy. A metal obstacle placed in the path of the rays quickly becomes incandescent, especially if the rays are focused upon it by using a concave cathode in the way already described. Much ingenuity has been expended by the makers of X-ray tubes in eliminating the very considerable production of heat at the point struck by the cathode rays. If the discharge is very powerful, portions of metal may be actually torn out of a solid plate by the impact of the rays.

A consideration of these facts leaves no doubt that the cathode rays consist of negatively charged particles. As we shall see these particles are identical with the electron, some of the properties of which we have already discussed. The supporters of the ether pulse theory relied mainly on the power of the rays to penetrate metal foil, and on the absence of electrostatic deflection. The latter objection was removed by the experiments just described, while the former vanished when it was shewn that the particles were not atoms but something many times smaller in size. In any case we now know that the objection was entirely illusory, though very reasonable at the time, as we have now direct evidence that even atoms such as those of

helium can under similar circumstances pass through solid matter without producing perforations.

By observing the combined action of an electric and a magnetic field upon the path of the particles it is possible to determine their velocity, and the ratio of the mass of the particle to the charge upon it

**46 Motion of a charged particle under the action of a magnetic field.** Let us assume that we have a stream of electrified particles moving with a velocity  $v$  along some direction  $OX$ . If each particle carries a charge  $e$  the total transference of electricity across any cross section of  $OX$  is  $ev$  per second, which is electrically equivalent to a current  $ev$  in the direction  $OX$ . This current will produce a magnetic field at a point in the neighbourhood, and conversely will be acted upon by a mechanical force if placed in a magnetic field.

The mechanical force on a current element of strength  $i ds$  in a magnetic field of strength  $H$  is equal to  $H i ds \sin \theta$ , where  $\theta$  is the angle between the direction of the current and the direction of the magnetic field, and acts in a direction perpendicular to these two directions. Putting the current  $i$  in the form  $dq/dt$  where  $q$  is the transference of electricity

$$\text{the mechanical force} = \frac{H dq}{dt} ds \sin \theta$$

Considering the case of a single particle,  $dq$  is the charge carried by the particle, while  $ds/dt$  is the velocity with which the particle is moving. Thus the mechanical force on the particle due to the magnetic field is equal to

$$Hev \sin \theta \quad . \quad . \quad . \quad (36)$$

in a direction at right angles to the velocity and the magnetic field

The magnetic equivalence of a moving electric charge to a current was demonstrated experimentally by Rowland. A large insulating disk was furnished near its circumference with a number of conducting studs which could be charged to a known value by induction from a neighbouring charged plate. On



rotating this disk at a rapid rate a magnetic field was produced, which was found to be, within the limits of experimental error, the same as that which would have been produced by a current of strength  $qv$  where  $q$  is the total charge on the studs, and  $v$  their velocity, if moving in a circuit coinciding with the path of the studs.

Suppose for simplicity that the particle is projected at right angles to the magnetic field (the mechanical force in this case is equal to  $Hev$ ). Since the mechanical force is always at right angles to the path of the particle the speed will remain unaltered. Let  $\rho$  be the radius of curvature of the path of the particle under the action of the field, and  $m$  its mass. The centrifugal force is equal to  $\frac{mv^2}{\rho}$  and for equilibrium this must be balanced by the mechanical force due to the field. Hence

$$\begin{aligned}\frac{mv^2}{\rho} &= Hcv, \\ \rho &= \frac{m}{e} \frac{v}{H}.\end{aligned}\quad (37)$$

As  $v$  is constant the radius of curvature is constant, that is, the particle describes a circle of radius  $\frac{m}{e} \frac{v}{H}$  in a plane at right angles to the magnetic field.

If the velocity of the particle has a component parallel to the magnetic field this component will remain unaltered since there is no mechanical force acting on the particle along this direction, and the particle thus moves forward through equal distances in equal times along this line, while at the same time describing a curved path around it. Its path is thus some kind of spiral, the axis of which is parallel to the field. If  $\theta$  is the angle between the direction of projection of the particle and the field we have

$$\begin{aligned}\frac{mv^2}{\rho} &= Hcv \sin \theta, \\ \rho &= \frac{mv}{eH \sin \theta}.\end{aligned}\quad (38)$$

Since  $v$  and  $\theta$  are constant  $\rho$  is constant and the path of the particle is a helix wound on a circular cylinder with its axis

parallel to the magnetic field and of radius  $r = \rho \sin^2 \theta = \frac{mv \sin \theta}{eH}$ .

When  $\theta = \frac{\pi}{2}$  this helix contracts into a circle, the case we have already considered.

In the general case, when the field is not uniform, the particles will describe spirals of varying amplitudes about the lines of the magnetic field

**47 Motion of a charged particle under the joint action of electric and magnetic forces.** If the particle is moving in an electric field of intensity  $X$  it will experience a force equal to  $Xe$ , and in the absence of any resisting medium, as for example when it is freely moving through a vacuum, it will have an acceleration of  $Xe/m$  in the direction of the electric field

If there is also a magnetic field it has, as we have seen, an acceleration  $H (e/m) v \sin \theta$  due to the magnetic field  $H$ , and its actual acceleration at any instant is the resultant of these two. The path will evidently depend on the magnitudes of the velocity, the magnetic, and the electric fields, and on their relative directions. The general solution has been obtained. It will, however, be sufficient to consider the cases which are of practical importance

**CASE 1** *The magnetic and electric fields act in the same line and the particle is projected at right angles to them.* In this case since the acceleration due to the magnetic field is at right angles to the field while that due to the electrostatic field is parallel to the field the two accelerations are at right angles to each other, and similarly the two deflections produced will also be at right angles to each other and to the path of the particle. Hence if the original velocity of the particle is so great that we may neglect the small change in its speed produced by the action of the electrostatic field on the particle, the deflection of the particle produced by one of the fields in the direction in which it acts will be independent of the action of the other. The final displacement of the particle will thus be the resultant of the two displacements which each would produce separately. For

example if the fields are arranged with their lines of force vertical, the electric field if acting alone would produce a vertical displacement of the particle of, say,  $y$  cm, while the magnetic field alone would produce a horizontal displacement of, say,  $x$  cm. Then if they are both acting together the particle will by their joint action be displaced to a position the co-ordinates of which will be  $x, y$ . This is the arrangement most generally employed in experimental work.

<sup>1</sup> CASE 2. *The electric and magnetic fields are at right angles to each other, and the particle is projected at right angles to the two fields.* In this case the mechanical force due to the two fields acts along the same line, and at right angles to the original velocity  $v$ . Thus the resultant force on the particle is equal to

$$Hev - Xe$$

assuming that the fields are so arranged that the forces are in opposite directions and acts along the direction of the lines of force of the electric field. This force will be zero if

$$Hev - Xe = 0$$

or

$$v = X/H. \quad . \quad . \quad . \quad (39)$$

The motion of the particle will in this case be unaltered by the joint action of the electric and magnetic fields, an important relation, which has often been used to determine  $v$ .

CASE 3 *A charged particle, initially at rest, is exposed to the joint action of electric and magnetic fields at right angles to each other.* Suppose the electric and magnetic fields coincide with the axes of  $X$  and  $Z$  respectively. The particle being charged will begin to move in the direction  $OX$ . As soon, however, as it has acquired a velocity it will be acted upon by the magnetic field, and its path will therefore be modified.

Suppose that at any instant the component of its velocity parallel to the electric field is  $dx/dt$ . There is then a mechanical force acting on the particle at right angles to the magnetic field and to the electric field, that is, in the direction of  $OY$ , and equal by (36) to  $Hedx/dt$ . Hence

$$m \frac{d^2y}{dt^2} = He \frac{dx}{dt} \quad . \quad . \quad (40)$$

The electric force along  $OX$  is equal to  $Xe$ , and there will also be a mechanical force in this direction due to the magnetic field equal to  $He dy/dt$ , where  $dy/dt$  is the component of the velocity of the particle along  $OY$ . Hence

$$m \frac{d^2x}{dt^2} = Xe - He \frac{dy}{dt} \quad (41)$$

The solution of equations (40) and (41) is

$$\left. \begin{aligned} x &= \frac{X}{\omega H} (1 - \cos \omega t) \\ y &= \frac{X}{\omega H} (\omega t - \sin \omega t) \end{aligned} \right\} \quad (42)$$

where

$$\omega = \frac{He}{m}$$

These are the equations to a cycloid, the curve traced out by a point on the circumference of a circle when the latter

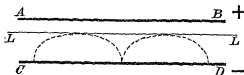


Fig. 38

rolls along a straight line. The path therefore consists of a series of loops as shown in Fig. 38, where the electrons are supposed to be liberated from the surface of the plate  $CD$ . It is obvious that the particle can never reach more than a certain distance in the direction of the electric field, and cannot penetrate beyond the plane  $LL$  which is the common tangent to the curves. Since the minimum value of  $\cos \omega t$  is  $-1$  this maximum distance is equal to  $\frac{2X}{\omega H}$  or  $\frac{2X}{H^2} \frac{m}{e}$ .

Thus if  $AB$  and  $CD$  are two parallel plates, and an electric field of strength  $X$  is established between them, while a uniform magnetic field  $H$  is applied at right angles to the plane of the paper, then if ions are formed on the surface of the negative plate  $CD$ , either by the action of ultra-violet light, or by raising it to incandescence or otherwise, no charge will be received by the

upper plate until it reaches the position  $LL$  in the diagram, at a distance  $d$  from the lower plate given by

$$d = \frac{2X}{H^2} \frac{m}{e}. \quad (43)$$

At any smaller distance the whole of the ions will reach the upper plate which will thus receive a charge.

The arrangement can therefore be used to determine the ratio  $e/m$ .

48. Thomson's method (3) of determining  $e/m$  and  $v$  for cathode rays. The simplest method of determining the important ratio of the charge of a cathode particle to its mass

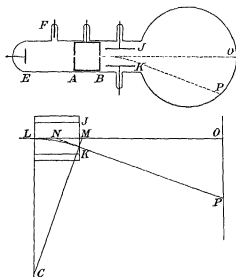


Fig 39

is based on the equations just developed. These principles receive their most direct application in the original experiments of Sir J J Thomson. The apparatus used is shown in Fig 39. The cathode  $E$  is a small aluminium disk, the anode  $F$  being placed in a side tube. A brass disk pierced with a small slit along the axis of the tube limits the rays to a narrow pencil, and to narrow the pencil still further a second brass disk

similarly pierced but with a still finer slit is placed at  $B$  some distance from  $A$ . A very fine flat pencil of rays is thus obtained which in the absence of any deflecting fields falls on a fluorescent screen of barium platino-cyanide or powdered willemite at the far end of the tube.

The electric field is applied by two parallel plate electrodes  $J$ ,  $K$ , their planes being parallel to the path of the rays. The lower plate is earthed while the upper is charged to a suitable potential by means of a large number of small accumulator cells. The field can thus be calculated if the distance between the plates is known. The deflection produced by the field on the negative particles of the rays is in the direction of the field, that is, in the plane of the paper.

The magnetic field is applied by a small electromagnet placed with its poles at right angles to the plates  $J$ ,  $K$ . Since the magnetic deflection is at right angles to the magnetic field the magnetic deflection is also in the plane of the paper.

Suppose now that both the magnetic and the electric fields are uniform and coterminous being applied over a short length  $LM$  of the path of the particles. The two fields produce deflections in the same straight line and by properly adjusting the sign and intensity of the electric field these two deflections may be made to neutralize each other, a condition the fulfilment of which can be ascertained by the return of the spot of light on the fluorescent screen to its undeflected position. Under these conditions we have by (39)

$$v = X/H$$

To find  $e/m$  for the particles we must now measure the deflection produced either by the magnetic or the electric field acting alone. Taking the former case the path of the particles while in the uniform field is bent into the arc of a circle of radius  $\rho$  given by

$$\frac{1}{\rho} = \frac{He}{mv}.$$

On emerging from the field at  $K$  the particles will continue to move along the tangent to the circle at  $K$ . The angle  $PNO$  through which the rays are deflected is by the geometry of the figure equal to the angle  $LCM$ , that is, to  $LM/\rho$ . Thus

$\frac{LM}{\rho} = \frac{OP}{ON}$  from which  $\rho$  can be determined when the deflection and the dimensions of the apparatus are known. Since the magnetic field and the velocity  $v$  are both known,  $e/m$  can be calculated.

The electrostatic deflection can also be calculated. The acceleration produced in this case is parallel to the field, that is, perpendicular to  $LO$  and equal to  $Xe/m$ . If the time during which the particle is in the field is  $t$  this produces a velocity  $X(e/m)t$  or  $\frac{Xe}{m} \frac{LM}{v}$  in a vertical direction. On leaving the field the particle moves with these two velocities. Hence if  $P'$  is the deflected position of the rays  $OP'/OM$  is equal to the ratio of the horizontal to the vertical velocity, that is, to

$$\frac{Xe}{m} \frac{LM}{v^2}, \quad (14)$$

which can be evaluated for  $e/m$  since the field  $X$  and the velocity  $v$  are known.

It is obvious that under the conditions of the experiment neither of the fields can be perfectly uniform owing to the disturbances near the edges of the plates and the poles. A correction can be applied as follows.

Since the curvature of the path is small we have approximately, if  $x$  is the co-ordinate of the particle measured along the undisturbed path  $LO$  and  $y$  the co-ordinate at right angles to it,  $\frac{1}{\rho} = \frac{d^2y}{dx^2}$ . Hence

$$\begin{aligned} \frac{d^2y}{dx^2} &= \frac{He}{mv}, \\ \therefore OP &= \frac{e}{mv} \int_0^{BP} \left[ \int_0^x H dx \right] dr. \end{aligned} \quad (15)$$

Similarly the electric deflection  $OP'$

$$= \frac{e}{v^2 m} \int_0^{BP} \left[ \int_0^x X dr \right] dx. \quad (16)$$

If these integrals are evaluated, which can be done when the distribution of the two fields is known, we have two equations for determining  $e/m$  and  $v$ .

49 **Kaufmann's method** (3) of determining  $e/m$  A somewhat different method was used by Kaufmann. In order to obtain a very uniform magnetic field of calculable value he enclosed the whole of the path of the cathode rays from the limiting aperture to the screen in a uniformly wound solenoid (Fig 40). The magnetic observations could thus be made with considerable accuracy. Instead of measuring the electrostatic deflection of the rays he assumed that the energy of the cathode particles was that due to a fall through the whole difference of potential between the cathode and the anode, that is, to  $Ve$  where  $V$  is the difference of potential between the electrodes of the discharge tube.

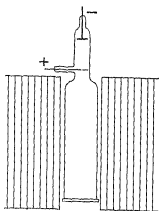


Fig 40

$V$  was measured by an electrostatic voltmeter. This assumption implies that the effect of the collisions of the rays with the residual gas is negligible. To test this point experiments were made for many different pressures of the gas in the tube. These different experiments were found to yield exactly the same results and hence, since the collisions would be relatively more frequent at high pressures than at low, Kaufmann's assumption seems justifiable. Hence we may write  $\frac{1}{2}mv^2 = Ve$ ,

$$v^2 = 2V \frac{e}{m} \quad . \quad . \quad . \quad (47)$$

A very careful investigation of the magnetic field was made and the integral (45) evaluated. In this way Kaufmann obtained a value for  $e/m$  of  $1.77 \times 10^7$  absolute e.m.u. per gm; a value very near the mean of the best recent observations.

50 **The magnetic spectrum** Since the velocity of the cathode particles depends on the difference of potential between the ends of the tube it will vary with the conditions of the experi-



ment In an ordinary discharge tube run by an induction coil the cathode rays are far from homogeneous since the potential difference between the terminals of a coil is not uniform but rises rapidly, at each interruption of the current, from zero up to a certain maximum Hence the cathode rays will contain particles having velocities corresponding to varying differences of potential from the minimum value necessary to produce the discharge up to the maximum value given by the coil. On applying a magnetic field, therefore, the single spot of light due to the undeflected beam will be drawn into a line at right angles to the lines of the field, each point of which will correspond to rays of a definite velocity. This effect is often known as a *magnetic spectrum*

51. **Numerical value of  $e/m$**  Though the values of  $v$  vary with the conditions of the experiment, the values obtained for  $e/m$  are invariably the same. Many experiments have now been made using different electrodes and different gases at different pressures. Experiments have also been made with other sources of electrons, such for example as the  $\beta$ -rays given off by radio-active bodies, the electrons emitted by heated oxides, and by the action of ultra-violet light on metals, all of which we shall consider later In every case, however, the value of the ratio  $e/m$  is within the limits of experimental error the same It is thus independent of all conditions and is a universal constant A few of the many results obtained are

TABLE III  
 $e/m$  for electrons from various sources

OBSERVER	SOURCE OF ELECTRONS	$e/m$ in c.m.u. per gm
Kaufmann	Cathode rays	$1.77 \times 10^7$
Classen	"	$1.771 \times 10^7$
"	Hot lime	$1.776 \times 10^7$
Pestelneyev	"	$1.766 \times 10^7$
Mal'ssez	Slow $\beta$ -rays from radium	$1.769 \times 10^7$
Woltz	" "	$1.767 \times 10^7$
Bucherer	" "	$1.763 \times 10^7$
Giesel	Zeeman effect (mean value)	$1.771 \times 10^7$

collected in Table III. It will be seen that the value of  $e/m$  does not differ appreciably from  $1.77 \times 10^7$  e.m.u. per gm which is the value we shall assume in this volume. Assuming that  $e$  has the value  $1.59 \times 10^{-20}$  c.m.u., the electronic charge, the value of  $m$  is  $9.0 \times 10^{-28}$  gm or about 1/1800 that of the hydrogen atom. The cathode particles are thus very small compared with the smallest atom hitherto known.

## 52. Direct measurement of the velocity of cathode rays

The velocity of the cathode rays has also been determined by direct experiment by Wiechert (1). The principle of the method is as follows. The cathode rays from a cathode  $C$  (Fig. 41) fall normally on a hole in a screen  $A$ , and through another hole in a screen  $A'$  on to a narrow fluorescent plate  $S$ . The rays are then deflected by a permanent magnet  $M$  placed near the cathode so that they all fall on the solid part of  $A$ , the screen  $S$

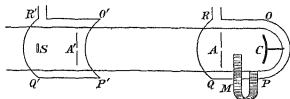


Fig. 41

in consequence being dark. A circuit  $OPQR$  carrying a rapidly alternating current such as that obtained by the discharge of a condenser is brought near  $AC$ , thus producing a rapidly alternating magnetic field. This will set the beam of rays swinging like a pendulum at right angles to the field, and if the force is sufficiently great the oscillations will be sufficiently large to reach to the hole in  $A$ . Thus rays will pass through intermittently, and the screen  $S$  will again become bright.

A second circuit  $O'P'Q'R'$  is now brought up near  $A'S$  carrying the same alternating current as that in the circuit  $OPQR$ . If the time taken by the rays to pass from  $A$  to  $S$  is zero the two magnetic fields will produce at any instant fields of the same sign and intensity, hence the rays between  $A'$  and  $S$  will suffer the same deflection as between  $C$  and  $A$  and

will be deflected off the screen which will thus be always dark. If, however, the time taken by the rays to pass from  $A$  to  $S$  is such that the current has changed its phase by one-quarter of a period during that time there will be no current in  $O'P'Q'R'$  when the rays reach  $A'$ . Thus the rays will suffer no further deflection and the screen will become bright.

Thus the screen will become bright if the time taken for the rays to describe a distance  $AS$  is equal to the time taken for the current in the wires to change by one-quarter of a whole period, that is, to  $\frac{1}{4}L/c$ , where  $c$  is the velocity of light and  $L$  the wave length of the current vibrations. The latter can be determined experimentally by any of the methods for determining wave lengths used in wireless telegraphy. Hence finally

$$v = AS \frac{4c}{L}$$

The values thus obtained were of the order  $3 \times 10^9$  or about one-tenth of the velocity of light. This result is of importance as proving directly that the cathode rays do not travel with the velocity of light and thus are not ether pulses.

**53 The positive rays.** We have seen that if a solid obstacle is placed in a discharge tube within the Crookes dark space it casts a shadow not only on the further walls of the tube but also on the cathode itself. This indicates that there are in the tube particles moving toward the cathode and, therefore, presumably positively charged. If a hole is made through the cathode normal to its surface these rays can be seen streaming through and causing phosphorescence in the residual gas behind the cathode. This phosphorescence is generally quite distinct in colour from that produced in the same gas by the cathode rays. In helium, for example, the path of the cathode rays is marked by a bluish light while that of the *Kanalstrahlen*, or *positive rays* as they are now called, is marked by a red glow.

The positive rays are now known to consist of positively charged molecules of the various gases in the discharge tube, moving with considerable speeds under the intense electric

field of the discharge. Their investigation proved a matter of great difficulty owing partly to the very intense ionization which they produce in the residual gases of the discharge tube, and partly owing to the secondary radiations to which they give rise. When a positive particle in the ray collides with a gas molecule, since the two are of comparable mass, it is frequently not the original particle but the molecule struck which continues the course of the rays, and this molecule may or may not be charged. Unless these effects are eliminated very curious and misleading results may be obtained. These effects may obviously be diminished by working at very low pressures so as to reduce the number of molecules of residual gas. On the other hand if the exhaustion is made very complete

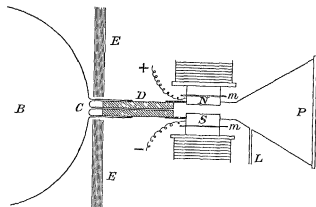


Fig. 42

it becomes a matter of very serious difficulty to obtain a discharge through the gas at all, and accurate measurements become impossible.

54. **Thomson's experiments on the positive rays** Professor Sir J. J. Thomson (5) was eventually after considerable research able to overcome these difficulties. One form of his apparatus is shown in Fig. 42.

The discharge takes place in a large bulb *B* of considerable size, it having been found that a discharge takes place much

more readily at very low pressures if the discharge tube is of considerable volume. At one time bulbs of 40 or 50 cms diameter were employed but it has since been found that a diameter of 20 cm is sufficient for the purpose. The cathode *C* consists of an aluminium rod with a rounded end, pierced by a very fine copper tube. This tube which was generally less than 1/10 mm in diameter, and in some experiments as little as 1/100 mm diameter, was made by drawing down ordinary narrow copper tubing through a draw plate. In this way when the discharge is passing an exceedingly fine pencil of positive rays is obtained. It is obvious that with a tube as narrow as 1/10 mm any stray magnetic field will deflect the charged particles constituting the rays against the walls of the tube where they will be lost. To prevent this the copper tube is enclosed in a thick tube *D*, of soft iron. Screens *E*, *E* also of soft iron are used to protect the main discharge.

Owing to the strength of the discharge considerable heat is produced at the cathode. It is therefore surrounded by a water jacket, not shown in the diagram, to keep it cool, and so to protect the numerous sealing wax joints in the neighbourhood.

The narrowness of the tube perforating the cathode serves a double purpose. It not only produces a very fine pencil of rays thus giving a very clear luminous spot on the phosphorescent screen or photographic plate placed at *P*, but it serves to separate very effectively the discharge tube *B* from the measuring apparatus, or camera as we may term it for brevity. Owing to the fineness and length of the tube which is the only connection between the two, diffusion takes place very slowly through it, especially at the low pressures used. If the camera is continuously exhausted through the side tube *L*, by a large tube of charcoal kept cool in liquid air, it is possible to have the gas in the camera at a considerably lower pressure than that in the discharge tube. Thus we can keep the pressure in the discharge tube at the value most suitable for the discharge, and at the same time maintain the vacuum in the measuring part of the apparatus so low that the positive rays are not seriously affected by the presence of residual gas. To keep the pressure in the discharge tube constant, fresh supplies of

the gas under experiment are introduced at a very slow rate through a side tube

To measure the velocity and the ratio of the mass to the charge for these particles, the same principles are employed as in the case of the cathode rays, the method adopted being that in which the two fields are applied in the same direction. The method of doing this, which is rather ingenious, is indicated in the figure. The pole pieces  $N$  and  $S$  are let into the sides of the chamber, the joints being made gas tight with sealing wax. They are electrically insulated from the core of the large electromagnet by thin strips of ebonite  $m, m$ . By connecting the magnetic pole pieces to the opposite poles of a large battery of small accumulators they can thus be used to apply the electrostatic field also.

Since the two fields are parallel the displacements they produce in the path of the rays will be at right angles to each other, the electrostatic displacement being in the plane of the diagram, the magnetic displacement at right angles to it.

In the final form of the apparatus the fluorescent screen  $P$  was replaced by a photographic plate. The positive rays affect the plate at the point where they strike it in the same way as light, so that on developing the plate the points struck by the particles appear as black spots or lines on the clear glass. The plate can then be placed under a travelling microscope and the deflections measured with accuracy.

The magnetic and electric displacements of a moving charged particle under the conditions of the experiment have already been calculated (§ 48). Taking the approximate formulæ of § 48, in which the fields are assumed to be constant over the whole of their extent, we should have, if  $x$  and  $y$  are respectively the electric and magnetic displacements of the particle,

$$x = Dd \frac{KE}{mv^2}, \quad y = Dd \frac{HE}{mv},$$

where  $D$  is the distance of the photographic plate from the field,  $d$  the length of the path of the particle in the field and  $E$

and  $m$  its charge and mass. Taking the accurate formulae (15), (46), we have

$$x = \frac{E}{mv^2} \int_0^{OP} \left[ \int_0^x X dx \right] dx, \quad y = \frac{E}{mv} \int_0^{OP} \left[ \int_0^x H dx \right] dx$$

The values of these integrals depend only on the applied field between the plates and the geometry of the apparatus. Hence for a given tube we can write them in the form

$$\left. \begin{aligned} x &= l_1 \frac{EX}{mv^2} \\ y &= l_2 \frac{EH}{mv} \end{aligned} \right\}, \quad . \quad . \quad . \quad (48)$$

where  $l_1$  and  $l_2$  are constants for a given apparatus and can be evaluated experimentally if required. Combining these equations we have

$$\frac{y}{x} = \frac{l_2}{l_1} \frac{H}{X} v, \quad (49)$$

$$\frac{y^2}{x} = \frac{l_2^2}{l_1} \frac{H^2}{X} \frac{E}{m}. \quad (50)$$

Thus if the two fields are maintained at a constant value throughout the experiment  $y/x$  is a measure of the velocity of the particle and  $y^2/x$  a measure of the ratio of the charge to the mass. The values of  $x$  and  $y$  can be obtained by measuring the co-ordinates of the deflected spot on the photographic plate

**55 Positive ray parabolas** Let us consider the matter in the light of equations (49) and (50)

If all the particles had the same velocity and the same value of  $E/m$  they would all be deflected to the same extent in the two fields, and the deflected rays would strike the screen in a single spot. Let us consider the production of the particles in the discharge. Some will be formed near the anode and will thus fall through the whole difference of potential between the cathode and the anode. Their energy will thus be  $VE$  where  $V$  is the difference of potential between the electrodes, and they will reach the cathode with a velocity  $v$  given by

$$\frac{1}{2}mv^2 = VE.$$

This is obviously the maximum velocity the particles can acquire. Those formed nearer the cathode will only fall through a fraction of this potential and will approach the cathode with smaller velocities. Hence the bundle of rays will contain particles of all velocities up to a certain maximum which will be a constant for the tube. Thus on applying the fields the single undeflected spot of light will be drawn out into a band on applying the two fields. It is obvious from equation (50) that all particles whatever their velocity for which the value of  $E/m$  is the same will lie on a single curve given by

$$y^2/x = \text{constant}$$

which is the equation to a parabola. If the stream of rays entering the two fields contains sets of particles for which the values of  $E/m$  are different, they will be sorted out into a series of parabolas, each of which corresponds to some definite value of the ratio  $E/m$ .

Again since the electric deflection  $x$  is given by  $x = k_1 \frac{EX}{mv^2}$ , and since the maximum value of  $v$  is given by  $\frac{1}{2}mv^2 = VE$  the smallest possible deflection we can obtain is given by

$$x = \frac{1}{2} k_1 \frac{X}{V},$$

and is constant for all the particles no matter what their mass and charge, if the deflecting field and the potential across the tube remain the same. Thus all the parabolas will stop abruptly at a line drawn parallel to  $OY$  at a distance  $\frac{1}{2} k_1 \frac{X}{V}$  from it.

If the magnetic field acts in the same direction throughout the experiment only one branch of each parabola will be obtained. By reversing the field half way through the experiment the direction of the deflection can be reversed and thus the lower half of the parabola can be obtained on the plate. This is always done in practice as it increases the accuracy with which the displacement can be measured. Thus on development the plate should have an appearance such as that shewn in Fig. 43, which represents the case of two sets of particles.

Two typical photographs taken by Sir J. J. Thomson by this



method are shewn in Figs 44*a* and *b*. It will be seen that the single undeflected spot is drawn out by the action of the fields into a series of curves one above the other which can be shewn by measurement to be parabolas. The curves in the lower half of the diagram are produced by reversing the magnetic field half way through the exposure, as already explained. It will be seen that they reproduce exactly the theoretical curves of Fig 43

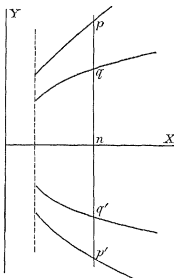


Fig 43

It is evident from equation (50) that the most deflected parabolas correspond to the greater values of  $E/m$ , that is, assuming all the particles to carry the same charge, to the lighter particles. Evaluating the constants it was found that the value of  $E/m$  for the most deflected parabola of all the values was almost exactly  $10^4$ . This as we have seen is the value of this ratio for the hydrogen ion in electrolysis. The most deflected parabola corresponds therefore to a hydrogen atom carrying a single electronic charge. To find the value for any other parabola we may proceed as follows. Draw any ordinate cutting the two parabolas (Fig. 43) in  $p, p'$  and  $q, q'$  and the axis of  $X$  in  $n$ . Then since  $x$  is the same for all points on the ordinate we have

$$\begin{aligned} \frac{(pp')^2}{(qq')^2} &= \frac{pm^2}{qn^2} = \frac{\eta_1^2/x}{\eta_2^2/x} \\ &= m_2/E_2 - m_1/E_1. \quad \dots \quad (51) \end{aligned}$$

If we can assume that the two sets of particles carry the same charge the ratio  $\frac{pp_1^2}{qq_1^2}$  measures the ratio of the masses of the two particles, or in other words if the outer parabola is that of

the hydrogen atom, the ratio gives the molecular weight of the particle forming the parabola

The matter is in general not quite so simple as this, since it is found that the particles in the positive rays may carry charges which are greater than the unit charge, that is, they may be atoms or molecules which have lost more than one electron. If they have lost  $n$  electrons the value thus deduced will be  $1/n$ th of the molecular weight. The method of procedure and the nature of the results obtained will be clear from the example given in Table IV which refers to a photograph taken with atmospheric nitrogen in the tube. The first column gives

TABLE IV

*Atmospheric nitrogen*

Potential across discharge tube, 30,000 volts, current through magnet, 3.5 amperes; potential difference between plates, 200 volts

$d$	$m/E$	NATURE OF PARTICLE	
7.2	200	Hg +	Mercury atom with single charge
10.3	100	Hg + +	Mercury atom with two charges
12.4	67	Hg + + +	Mercury atom with three charges
15.4	44	CO <sub>2</sub> +	Molecule of carbon dioxide
16.5	39	Ar +	Argon (40) with single charge
19.4	28	N <sub>2</sub> +	Nitrogen molecule with single charge
23.1	20	Ne +	Neon with single charge
25.6	15.9	O +	Oxygen atom with single charge
27.6	14	N +	Nitrogen atom with single charge
30.0	12	C +	Carbon atom with single charge
38.7	7	N + +	Nitrogen atom with double charge

the distance  $pp'$  between the two limbs of the same parabola (which are obtained as already explained by reversing the magnetic field in the middle of the exposure), the second column the value deduced for the ratio  $m/E$ , the value for the hydrogen parabola being taken as unity. It therefore gives the molecular weight of the particles forming the parabola assuming them to have the unit charge. The last column gives the origin assigned to the particles, a double electronic charge being expressed by two plus signs (+ +), and a triple charge by three. It will be seen that the rays contain atoms and

molecules of nitrogen together with other atmospheric gases such as argon and neon, carbon dioxide and carbon, probably from the grease used on the taps, mercury vapour from the pump, and oxygen, probably due to moisture. The hydrogen parabola has been deflected off the picture altogether.

It will be noticed that in several instances it is necessary to suppose that the particles carry twice or three times the unit charge. In the case of mercury as many as eight units of charge are occasionally met with giving a parabola the value of  $m/E$  for which is 200/8 or 25. The parabolas formed by the multiple charged atoms are always less distinct than those due to the same carriers with single charges. This result is often of value in enabling us to determine the origin of a given parabola, for example to distinguish between a singly charged atom of nitrogen and a doubly charged molecule of carbon monoxide, which would give the same value for  $m/E$ . In some cases however the uncertainty cannot be cleared up except from a consideration of the gases most probably present in the tube under the conditions of the experiment.

**56. Negative parabolas** In some of the positive ray photographs parabolas are seen in the opposite quadrant to those we have just been considering. These give the same values for  $E/m$  as those in the first quadrant but it is obvious that the particles must carry negative instead of positive charges, since both the electrostatic and the electromagnetic deflections are in the opposite direction to those for the positive particles. Since these particles have come through the cathode it is also evident that they had a positive charge while in the discharge but that this charge had been not only neutralized but reversed before reaching the deflecting fields, that is, during their passage along the fine copper tube. It must be remembered that the positive rays produce ionization in the residual gas through which they pass and hence are surrounded by negative electrons. If the positive particle acquires two of these during its passage down the tube it will have a unit negative charge when it emerges and hence will give rise to a negative parabola. If only one is taken up it emerges uncharged and is

then undeflected by the fields. This is probably the fate of the majority of the particles in the rays since there is always an undeflected spot on the plate as shewn in the photographs in Figs. 44 *a* and *b*, which is generally much more intense than any of the parabolas. The negative parabolas are most marked in the case of oxygen and the halogens, as we should perhaps expect, these elements being markedly electro-negative in character. Strangely enough the phenomenon also occurs with the hydrogen atom. It has never been observed with nitrogen or helium.

**57. Positive ray analysis.** The method can obviously be employed to analyse a given gas, at any rate qualitatively. For this purpose it is far more sensitive than the spectroscopic method which has hitherto been the most delicate known. The sensitiveness of the method is demonstrated by the following facts. Photographs taken with atmospheric argon in the tube at a pressure of 1/300 mm. of mercury always shewed the helium parabola quite distinctly. The volume of the discharge tube was about two litres so that the volume of argon under experiment would have a volume of about 1/100 c.c. at atmospheric pressure. This is the amount present in 1 c.c. of air. We can thus detect the helium present in a single cubic cm. of ordinary air. According to Ramsay this is of the order of four millionths of a cubic cm. The experimental difficulties are, however, great and the method is not likely to come into general use.

The importance of the method is that it measures the masses of individual particles, whereas chemical methods of determining atomic weight give only the average mass of the atoms of an element, all the atoms of the same element being assumed to be identical. Sir J. J. Thomson has shewn that the neon line (atomic weight 20) is always accompanied by a fainter line corresponding to an atomic weight of 22. The substance forming this line is inseparable from neon by any chemical treatment. Radio-active theory (§ 139) had already suggested the possibility of the existence of substances identical in chemical properties, but differing in atomic weight. Such substances are called isotopes. Thomson's experiments suggest strongly that the existence of isotopes is not confined to the radio-active elements but that

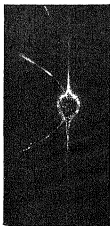


Fig 44 a



Fig 44b  
Positive Ray Parabolas



Fig 45  
L Spectrum of  
Tungsten  
(Photograph by  
Dr G Shearer)  
(See note on p 116)



Fig 46  
Mass Spectrum  
of Chlorine  
From Aston's  
Isotopes)



neon consists of a mixture of two isotopes having atomic weights of 20 and 22

The method may also have applications in the study of chemical decomposition. Owing to the fact that the particles register themselves on the plate in a time which is generally considerably less than a millionth of a second, very unstable combinations of atoms may be found among the particles in the positive rays. Thus, if the tube contains methane, parabolas are found representing not only methane itself and its constituents carbon and hydrogen but also the intermediate stages  $\text{CH}$ ,  $\text{CH}_2$  and  $\text{CH}_3$ .

Only certain elements seem capable of entering directly into the positive rays. The metals are noticeably absent. Mercury always gives well-marked parabolas if present even in minute traces, and nickel has been obtained when nickel carbonyl is introduced into the tube, but only with much difficulty. The other volatile metallic compounds give no trace of their metallic constituent among the positive ray parabolas produced. If, however, the anode is made of wire coated with the oxide of a metal, and raised to incandescence by passing a suitable current through it, positively charged atoms of the metal are emitted by the anode (§ 67) and these anode rays can be treated in exactly the same way as the ordinary positive rays.

**58 The mass-spectrograph** **Aston's experiments** By an ingenious modification of the original method, permitting the use of much greater dispersions without loss of intensity, Aston (6) has been able to measure the masses of the atoms in the positive rays with an accuracy which compares favourably with that attained in chemical measurements of atomic weight. In the original experiments already described the positive particles having the same value of  $e/m$  but differing in velocity are scattered along a parabolic curve of considerable length. The intensity at any point on the curve is therefore small, and if the original beam of rays is at all fine very prolonged exposures are required to obtain a measurable trace on the plate. If the particles of different velocity but the same mass could all be focused on the same spot it is obvious that a much finer pencil

of rays could be employed, together with much greater dispersion, without at the same time making the necessary exposure unduly long.

This has been achieved by Aston in the following way. A narrow pencil of positive rays is passed first through the electric field between a pair of parallel plates and is thus spread out into what may be called an electric spectrum. The deflection  $\theta$  of a given particle is given by equation (41), § 48. If the deflections are sufficiently small we may write  $OP'/OM = \theta$ , whence

$$\theta v^2 = X \cdot LM \cdot \frac{e}{m} = XI \cdot \frac{e}{m} \text{ if } LM = l.$$

The deflected rays then pass through a magnetic field, arranged so as to produce a deflection of the rays in the opposite direction to that of the electrostatic field. The deflection  $\phi$  produced is obviously equal to  $L/\rho$  where  $L$  is the length of the path in the magnetic field and  $\rho$  the radius of curvature produced (see Fig. 39). Hence by equation (37) we have

$$\phi v = L \cdot H \cdot \frac{e}{m}.$$

Now in a given experiment  $X$ ,  $H$ ,  $L$  and  $l$  are constant. Hence for all particles which have the same value of  $e/m$ , we have, by differentiating

$$\frac{\delta\theta}{\theta} + \frac{2\delta v}{v} = 0, \quad \frac{\delta\phi}{\phi} + \frac{\delta v}{v} = 0,$$

$$\frac{\delta\theta}{\delta\phi} = 2 \frac{\theta}{\phi}.$$

Now  $\delta\theta$  and  $\delta\phi$  represent the change in the deviation produced by the electric and magnetic fields of particles having the same  $e/m$  when their velocity differs by  $\delta v$ . These differences will be equal if the mean electric deflection  $\theta$  is one-half the mean magnetic deflection  $\phi$ . Since the deviations are in opposite directions the total deviation would be zero and the rays would emerge as a parallel beam. Owing to the dispersion produced by the electric field, however, this beam would have a finite width. By increasing the magnetic deviation this beam can be brought to a focus.



Let us suppose for simplicity that the electric field can be supposed concentrated at a point  $Z$  (Fig. 47) and the magnetic field at a point  $O$ . Then  $ZOP$  will be the path of one ray and  $ZO'P$  that of another of the same mass but of different velocity. Then since  $\theta$  and  $\phi$  are both very small angles in practice, we have

$$OO' = OZ \quad \delta\theta = OP \quad \delta(\phi - \theta).$$

$$\frac{OP}{OZ} = \frac{\delta\theta}{\delta(\phi - \theta)} = \frac{2\theta}{\phi - 2\theta}$$

by the previous equation. Now in all cases the particles are most numerous near the heads of the different parabolas. The mean kinetic energies of the different kinds of particles will be

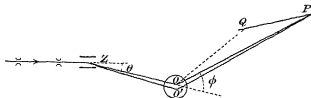


Fig. 47

therefore very much the same (p. 106) and the average value of the electrostatic deflection will be the same for all kinds of particles. Thus  $\theta$  is approximately constant and

$$OP(\phi - 2\theta) = OZ \quad 2\theta = \text{constant}$$

This gives the locus of the foci of rays of different masses. This is approximately a straight line making an angle of  $2\theta$  with the direction  $ZO$  and passing through the point  $Q$  for which  $OQ = OZ$  and the magnetic deflection  $\phi = 4\theta$ . A photographic plate placed along this line will be in focus for a very fair range of different masses, each different kind of particle being brought to its own focus. The fineness of the focusing and the dispersion obtainable are shown in Fig. 46 which is reproduced from one of Aston's plates.

Thus particles having the same value of  $e/m$  are brought to a single point, instead of being spread over a parabolic arc. Extremely narrow beams can be employed, and the position of lines obtained can be measured to an accuracy amounting in the case of a good plate to one part in a thousand.

The results have proved most interesting. Taking the mass of the oxygen atom as 16.00 the mass of every other particle as registered on the plates is also an exact whole number. Elements whose accepted weights, on the basis of  $O = 16$ , differ from whole numbers are found on investigation to consist of mixtures of isotopes, each of which has a whole number for its atomic weight. Thus neon (20.2) consists as we have seen of a mixture of gases of identical chemical properties but having atomic weights of 20 and 22. Chlorine (35.4) is a mixture of atoms of mass 35 and 37, while Krypton (83) appears to be a mixture of no less than six isotopes with integral values for their atomic weights ranging from 78 to 86. These differences in mass extend to the molecular weights of the compounds of the different isotopes. Thus if hydrochloric acid is introduced into the discharge tube particles are obtained with masses 36 and 38 (Fig. 46) corresponding to the hydrogen compounds of the two isotopic chlorines. If the gas in the discharge tube is complex practically every position on the plate corresponding to an integral value of the mass may be occupied by a line, and the regularity of the spacing of these lines is very striking.

Only one exception to the rule has so far been observed, namely hydrogen, the mass of which, on the basis  $O = 16$ , is found by the positive ray measurements to be 1.008, which agrees closely with chemical determinations. All these facts find a ready explanation on Rutherford's theory of the atom (§ 147).

**59. Electrical method of measuring positive rays.** Since the particles carry positive charges it is possible to detect them electrically. For this purpose the screen *P* (Fig. 42) is replaced by a thick brass plate *B* (Fig. 48) in which a parabolic slit *SS* is cut at some distance from the centre. A small Faraday cylinder is fastened behind the slit as shewn in Fig. 48 (*b*), the inner cylinder being connected to a sensitive electroscope. Keeping the electric field constant the magnetic field is gradually increased so that each parabola in turn, in moving out from the axis of *X*, passes over the slit in the plate. The passage of each parabola across the slit is marked by a deflection in the electro-

scope. If the current is measured the relative number of particles in each parabola can be determined. The value of  $m/E$  can be deduced from the corresponding values of the fields, remembering that the value of  $y^2/x$  is now fixed by the position of the slit. If the slit is made sufficiently narrow, the parabolas due to particles differing by only one or two units of atomic weight can easily be distinguished.

The results obtained shew that the photographic method may be very misleading if the relative darkness of the various lines is taken as a criterion of the relative number of particles going to form the parabolas. For some unexplained reason the atoms of the elements of low atomic weight produce far more effect on a photographic plate than an equal number of atoms

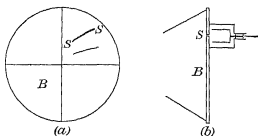


Fig 18

of a heavier element. Thus the hydrogen parabola may often be the most intense on the plate although the number of hydrogen atoms in the rays is shewn by the electrical method to form no more than one per cent. of the whole (7).

**60 Secondary effects.** Lines which are not parabolic are sometimes found on the plates. These are generally due to particles which have lost their charge while actually in the two fields. Their deflection, therefore, has a value intermediate between that of a charged and an uncharged particle. These secondary effects can generally be recognized as such by repeating the experiments at a slightly lower pressure, when owing to the smaller number of molecules available for collisions they either disappear or at any rate alter their appearance or position. Unless they are carefully watched for they are apt to give rise to misleading results.

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NOTE ON FIG 45 The plate was taken with the crystal making complete revolutions The spectrum thus appears symmetrically, both above and below the wide central patch, which marks the position of the undeviated portion of the incident beam The critical  $K$  absorption limits of bromine and silver (contained in the emulsion) can be seen in the continuous background as the increased absorption of the rays at the critical frequencies causes increased blackening of the negative at these points The figure is a positive print from the negative

## CHAPTER VIII

### EMISSION OF ELECTRICITY BY HOT BODIES

61    **Loss of charge from a hot body.** The fact that heated bodies are unable to retain electric charges has been known for nearly two centuries. Thus it was found that a red-hot iron ball was unable to retain a positive charge but would retain a negative one, while at higher temperatures still it was unable to retain a charge of either sign. The early experiments were not made under very definite conditions and most of our knowledge of the phenomena is due to experiments made since 1900, and very largely to the work of O. W. Richardson, who has given the name *thermionics* to this branch of the subject. The current from a heated body is thus known as the *thermionic current*, while the carriers by which the discharge is carried are known as *thermions*. As we shall see the negative carriers are negative electrons, while the positive carriers are positively charged atoms. The terms are however very convenient, and will be retained.

The phenomena are in general very complex, the current depending on the nature and pressure of the surrounding gas, and on the nature and previous treatment of the heated substance. To simplify matters as far as possible we will take the case of a metallic wire which has been carefully treated to remove impurities, heated in a high vacuum so as to eliminate all effects due to the presence of gas. The effect can be studied conveniently with the apparatus shewn in Fig. 49. The wire *AB* to be heated is surrounded by an outer metal cylinder *CC* which remains cool during the experiment, the whole being enclosed in a glass vessel which can be evacuated. The wire is heated by a current from an insulated battery of cells and the temperature of the wire can be estimated by measuring its electrical resistance and thus making it serve as

its own resistance thermometer. If the wire is raised to a suitable small potential a current flows from the hot wire to the cool cylinder. This current can be measured either by the electrometer method, or in many cases simply by allowing it to flow to earth through a galvanometer.

Initially with a new wire the current will flow through the tube whether the wire is negatively or positively charged shewing that thermions of both signs are emitted. If, however, the wire is kept glowing for some time and the gases evolved from the heated wire are continually removed by pumping, or better still by sweeping them out with pure oxygen, it is found that the positive current rapidly decreases and finally becomes negligibly small. The negative emission is also much reduced by this process but finally settles down to a steady value. In a good vacuum the thermionic current is independent of the

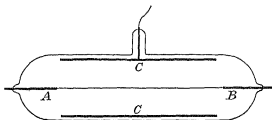


Fig. 49

potential difference if the latter exceeds a few volts. The maximum current between the electrodes under given conditions is known as the saturation current by analogy with the case of the current through ionized air. The temperature to which the wire must be raised for an appreciable current to flow depends on the nature of the substance. For platinum a temperature of about  $1000^{\circ}\text{C}$  is required, for sodium on the other hand there is a very considerable thermionic emission at temperatures as low as  $300^{\circ}\text{C}$ .

**62 Nature of the negative thermions** The value of the ratio  $e/m$  for the negative thermions emitted by a hot wire can be determined by making use of equation (43), § 47(1). A measured difference of potential is applied between the hot

wire and the outer cylinder and a magnetic field is applied at right angles to the electrostatic field and parallel to the electrodes. The value  $H$  of the magnetic field which is just sufficient to prevent the thermions reaching the cold electrode is found whence

$$\frac{e}{m} = \frac{2V}{H^2 d^2}$$

where  $V$  is the difference of potential between the electrodes and  $d$  their distance apart. In this way a value of  $1.6 \times 10^7$  was obtained for  $e/m$  for the negative thermions, agreeing as well as could be expected with the value of the same ratio for an electron.

**63 Variation of the current with temperature** The thermionic current increases very rapidly as the temperature of the wire is increased. Richardson (2) has found that in every case the relation between the saturation current and temperature can be represented by an equation of the form

$$i = A\theta^2 e^{-\frac{b}{\theta}} \quad (52)$$

where  $A$  and  $b$  are constants for a given substance. This relationship applies to all cases of thermionic emission, not only to that of pure metals, but also to cases such as that of carbon, and heated oxides where the current is often over a thousand times greater than that from, say, pure platinum. It thus represents a very fundamental property of thermionic emission. The relation is represented graphically by the curve of Fig. 50 which is drawn for the case of a platinum wire, the constants for which were

$$A = 6.9 \times 10^7, \text{ and } b = 65,000.$$

For pure platinum in a good vacuum the observed current was at  $1375^\circ \text{C}$ ,  $1.57 \times 10^{-8}$  amperes per square cm. of area, and at  $1500^\circ \text{C}$ ,  $128 \times 10^{-8}$ . The calculated values using the above constants are respectively  $1.49 \times 10^{-8}$  and  $123.5 \times 10^{-8}$ . The results agree to within a few per cent.

**64. Theory of thermionic emission** Let us assume that a conductor contains scattered through its volume a large

number of free electrons. There is much evidence for this view. It will, for example, enable us to account for the conductivity of the conductor by assuming that the electrons move through the metal under the action of the electric field in the same way that the gaseous ions move through a gas. The existence of these free electrons has also been postulated to explain the Peltier effect, the Thomson effect and various optical phenomena.

Let us assume also that the electrons in the metal behave like the molecules of a perfect gas. Since the spaces between the atoms are large compared with the radius of an electron this assumption seems justifiable. In this case the electrons will be moving with the kinetic energy characteristic of the temperature of the substance in which they find themselves. Their velocity will therefore increase as the square root of the absolute temperature. Thus the mean velocity of the electrons at an absolute temperature  $\theta$  is given by  $\frac{1}{2}mv^2 = a\theta$ , or

$$v = \sqrt{\frac{2a\theta}{m}}, \quad \dots \quad (53)$$

where  $a$  is a constant which is the same for all gases.

While the electrons are in the metal they are perfectly free to move, except in so far as their motion is changed by collisions with atoms of the metal or with other electrons. If, however, an electron passes the surface, its charge will induce an opposite charge on the surface of the metal and work must be done to carry the electron completely away from the surface against the mutual attraction of the two charges.

The electron will succeed in escaping if its kinetic energy

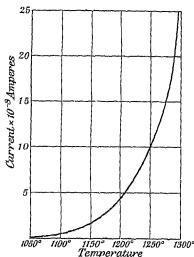


Fig. 50



in a direction normal to the surface is greater than the work  $w$  which must be done in separating the electronic charge from the surface, that is, if  $\frac{1}{2}mv^2 > w$ .

The velocities of the electrons will be distributed about the mean in the way given by Maxwell's distribution law. Theoretically there should at any temperature be occasional electrons possessing the necessary velocity, but at ordinary temperatures these will be very few. As however the temperature is raised the value of the mean velocity increases and hence the number of electrons possessing the minimum energy increases too, and the number escaping increases at a rapid rate. If the electrons remain in the space around the metal, they will accumulate until their pressure is so great that the number returning to the metal surface is equal to the number leaving it. We can easily find the ratio of the numbers in the two media when equilibrium is established.

If  $n$  is the number of electrons in unit volume,  $p$  the pressure of the electrons and  $X$  the electric force acting on an electron, the total force acting per unit volume must be equal to the rate of change of pressure. Thus

$$\frac{dp}{dx} = Xn$$

But  $p = \beta\theta n$  by the kinetic theory where  $\beta$  is a constant which is the same for all gases. Thus

$$\beta\theta \frac{dn}{dx} = Xn \quad . \quad . \quad (54)$$

Let us integrate the equation from a plane within the metal surface to a parallel plane outside it. Then if  $n'$  is the number of electrons per unit volume in the space above the metal,  $N$  the number in the metal itself,

$$\begin{aligned} \beta\theta \log \frac{n'}{N} &= - \int X dx = -w, \\ n' &= N e^{-\frac{w}{\beta\theta}}, \end{aligned} \quad (55)$$

where  $w = \int X dx$  is the work which must be done to drag an electron out of the metal.

The number of electrons returning to the metal surface per unit area per second can easily be calculated from the kinetic theory. If we make the usual elementary assumption that the number of particles travelling in each of the six directions parallel to the faces of a cube is one-sixth of the number present in the gas, and that all the particles possess the mean velocity  $v$  for the temperature, the number  $n_0$  striking the surface per unit area in one second will be all which are travelling normal to the surface whose distance from the surface is less than  $v$ , that is,  $n'v/6$ . Substituting for  $v$  its value in terms of  $\theta$  we have

$$n_0 = \frac{n'}{6} \sqrt{\frac{2\alpha\theta}{m}} \quad (56)$$

The more correct value, taking into account the distribution of velocities among the particles, can be deduced from the kinetic theory. It differs only from the one given by a numerical constant. Hence we have

$$n_0 = Cn'\theta^{\frac{1}{2}} \quad (57)$$

where  $C$  is some constant for the electrons.

Now in the equilibrium state which we have been considering the number of electrons leaving the surface is equal to that returning to it. Also the number leaving the metal depends only on the conditions in the metal and not on the presence or absence of external electrons. Hence the number of electrons leaving unit area of a metal at a temperature  $\theta$  is given by

$$\begin{aligned} n_0 &= Cn'\theta^{\frac{1}{2}} \\ &= C\theta^{\frac{1}{2}} N e^{-\frac{w}{\rho\theta}} \end{aligned} \quad (58)$$

The current is  $n_0 e$  since each electron carries a charge  $e$ . This is obviously of the form of the experimental curves provided that  $N$ , the number of free electrons per unit volume of the metal, is independent of the temperature.

### 65 Evidence for the theory of thermionic emission

The hypothesis thus developed is capable of experimental verification in many ways. For example, since work is done in extracting the electron there should be a cooling of the wire when thermions are emitted. Thus more energy should be required to keep the wire at a given temperature if the

thermions are allowed to escape than if they are all kept in the wire by the application of a retarding electric field. This effect has been investigated by Richardson<sup>(3)</sup> and is found to be of the magnitude demanded by the theory. The reverse effect of the production of heat in a wire when thermions are absorbed by it has also been investigated and found to agree with the theory.

A still more satisfactory proof of the theory is afforded by the measurement of the distribution of velocities among the thermions emitted by the wire. Since the velocities of the electrons in the metal are distributed according to the Maxwell-Boltzmann law, it can be shown by the ordinary analysis of the kinetic theory that the velocities of the thermions which escape after parting with the definite amount of energy necessary to liberate them from the metal should also be distributed in the same way. This has also been investigated by Richardson<sup>(4)</sup> by a method based on the following principle.

Let the cool electrode be maintained at a definite negative potential  $V$ . The work done by the negative electron in passing from the surface of the hot strip to the negative electrode will thus be  $Ve$ , and the electron will only succeed in reaching the electrode and imparting its charge to it if the kinetic energy  $\frac{1}{2}mv^2$  is greater than  $Ve$ .

Thus the current reaching the electrode is a measure of the number of thermions whose kinetic energy perpendicular to the strip is greater than  $Ve$ . In this way the distribution of normal velocities of the thermions can be studied. A slight extension of the method can be used to measure the distribution of the velocities of the thermions in a direction parallel to the surface of the hot strip. In both cases the distribution found agreed very closely with that deduced from the Maxwell-Boltzmann law. This experiment is of great interest, not only as evidence for the hypothesis of thermionic emission but also as affording a direct proof of the validity of the assumptions of the kinetic theory of gases.

**66. Discharge of negative electricity by various substances.** The negative thermionic current is peculiarly sensitive

to the presence of various gases, and notably of hydrogen. The admission of a very minute quantity of hydrogen into the vacuum chamber, or even its previous absorption by the wire, is found to increase enormously the current from the wire. If hydrogen at a pressure of no more than 0.0006 mm. of mercury is admitted into the vessel the current from glowing platinum at a temperature of  $1350^{\circ}\text{C}$  is increased no less than 2500 fold. The relation between temperature and current is still of the form given in (52) but the constants are both reduced, the value of  $A$  being reduced to  $10^6$ , while that of  $b$  is reduced to 55,000. A reduction in  $A$  by itself would diminish the current. Owing however to the form of the equation the current depends principally on the value of  $b$ , and the small reduction in  $b$  is more than sufficient to outweigh the very considerable decrease in  $A$ .

The effect is probably due to the condensation on the platinum of a layer of hydrogen. Hydrogen is a very electro-positive element, and if we assume that the hydrogen atoms in the condensed layer are positively charged their presence will produce a field between the gas and the metal tending to assist the escape of the electrons from the metal. Less work will thus be required to extract an electron from the metal. Since  $b$  is proportional to this work the value of  $b$  will be decreased, as is actually found to be the case. The reduction in  $A$  is probably bound up in some way with that in  $b$ .

For some solids the thermionic emission attains values very much greater than those obtained for pure metals in a vacuum. Thus ordinary carbon as used in carbon filament lamps gives a negative emission which even in a good vacuum may attain the order of several amperes per square cm. This effect which is known as the Edison effect has been used by Fleming to rectify the alternating currents set up in wireless receivers by the action of the wireless waves. The effect in carbon is however due to impurities. Pure carbon has been found to give thermionic currents much smaller even than those from pure platinum.

The modern triode valve works on the same principle when used as a rectifier, and valves, on this principle, capable of rectifying currents of half an ampere are now procurable, the

cathode being a filament of tungsten at a temperature of about  $2200^{\circ}\text{C}$ . The emission at this temperature is about 1 ampere per sq. cm.

The effect is also very marked in the case of certain metallic oxides, and notably those of calcium, barium and strontium. Thus while pure platinum in air at low pressure gave a thermionic current of about  $5 \times 10^{-7}$  amperes per square cm. of surface, the thermionic current from lime at the same temperature was  $5 \times 10^{-2}$  amperes per sq. cm., and for lime in an atmosphere of hydrogen no less than 1000 amperes per sq. cm.

A strip of heated platinum coated with a small speck of lime thus furnishes a very convenient source of electrons and is known as a *Wehnelt cathode*. The strip of foil carrying the

TABLE V

	<i>A</i>	<i>b</i>
Platinum	$11.5 \times 10^4$	51,000
Tungsten	$24 \times 10^4$	52,500
Molybdenum	$22 \times 10^4$	50,000
Thorium	$2 \times 10^5$	39,000
Calcium	$1.76 \times 10^4$	36,500
Sodium	$1.6 \times 10^{12}$	31,600
Lime	$6.9 \times 10^7$	40,000
Barium	$1.2 \times 10^7$	45,000

speck of oxide is heated by a current from an insulated battery, and a suitable potential is applied between the strip and the anode in the tube to give the electrons the desired velocity. Under these circumstances a pencil of cathode rays is given out by the lime, which if the pressure of the gas is not too low is made visible by a blue phosphorescence in the gas along the path of the particles. The deflection of these rays in the magnetic and electric fields can readily be demonstrated, and the value of  $e/m$  determined. As we have already seen (Table III) it is the same as that for the rays from an ordinary cathode.

The negative emission from these substances obeys the same temperature law as that from hot platinum. The value of  $b$  is, however, generally much smaller. The great emission is

therefore due to the smaller amount of energy necessary to extract an electron from the surface of these substances. The values of  $b$  and  $A$  for a few substances are collected in Table V. These figures refer to electrodes heated in a high vacuum.

It must be noted that many of them are very uncertain, the results of different observers differing within very wide limits. This is undoubtedly due to the presence of minute quantities of gas during the experiments. Owing to their commercial importance tungsten and molybdenum have been studied with the greatest care and with modern high vacuum technique, and the values here are concordant to within a very few per cent.

**67 Discharge of positive electricity.** We have already noted that if a new wire is used for the experiment there is an emission of positive electricity from the wire. This emission is noticeable at temperatures considerably lower than those necessary to produce a measurable negative current from the wire. It is quite easily detectable at a temperature of  $800^{\circ}\text{C}$ . The exact method of formation of the positive carriers is unknown. The temperature variation of the current, however, follows the same law as that for the negative carriers, and the process may perhaps be regarded as analogous to some sort of evaporation from the surface of the metal.

The value of  $e/m$  for the positive carriers can be measured by the method already described for the negative thermions (§ 62). If the experiment is performed in a good vacuum the value of  $e/m$  for the positive carriers seems to be independent of the nature of the heated metal (7). Experiments made with, amongst others, platinum, manganese, tungsten, and steel, all gave values of  $e/m$  for the positive thermions of the order of  $250\text{ e m u per gm}$ . The value of this ratio for the hydrogen ion in solution is as we have seen approximately  $10^4$  in the same units. Hence if the charges can be assumed to be the same in the two cases, that is, if the positive thermions are only singly charged, the mass of the thermionic positive carriers is about 40. Exactly the same value was obtained when the wires were coated with potassium sulphate. The effect, therefore, seems to be due to the presence of traces of potassium.

After a very prolonged heating atoms of mass 23 were also observed. These are probably sodium.

In the absence of gas the positive thermionic current gradually disappears with continued heating. It is restored if the wire is removed and exposed for some days to the atmosphere of the laboratory. If, however, the tube contains gas at appreciable pressure the thermionic positive current persists and in this case a measurement of  $e/m$  for the carriers shews that they consist of the atoms and molecules of the gas in the tube.

Salts of the alkali metals give large positive emissions(s). In this case the carriers are always atoms of the metal in the salt, thermions having masses corresponding to the atoms of lithium, sodium, potassium and rubidium having been obtained from the corresponding salts. Certain phosphates also give large positive emissions. In this case the carriers appear to be molecules of carbon monoxide.

**68 The current through a thermionic valve. Langmuir's Law** Richardson's Law (52) gives the relation between the temperature and the saturation current from a heated filament. In the earlier experiments where the currents measured were small saturation was easily obtained with potential differences of a few volts only. This is by no means the case in a modern thermionic valve. Langmuir(s) has shewn that if a constant potential difference is maintained between the electrodes and the temperature of the hot wire is gradually increased the current at first increases in accordance with the law of Richardson. Soon however the rate of increase with temperature becomes rapidly smaller than that given by the law and eventually the current reaches a maximum value which then remains constant however much the temperature may be increased, as illustrated in Fig. 51. This constant current, however, depends on the potential difference employed, and if  $V$  is this potential difference the value of the constant current  $i$  is given by

$$i = kV^{\frac{1}{2}} \quad (59)$$

This is known as Langmuir's law.

This limitation of the current is due to the presence between the electrodes of the negative electrons which are carrying the current. These negative charges will repel the negative electrons which are tending to emerge from the hot cathode and, as the current grows bigger and hence the number of electrons in the space becomes more numerous this repulsion increases until finally it counterbalances the applied field, and the actual field at the surface of the cathode becomes zero or may even be reversed. At this point emission from the hot wire would cease. The maximum current which can pass for a given potential difference is thus limited by the space charge due to the electrons between the electrodes.

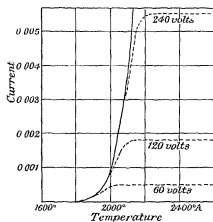


FIG. 51

We may take as a simple case a pair of parallel plates at a distance  $d$  apart, the heated plate being at potential zero and the cold plate at a positive potential. Then if  $\rho$  is the space charge (charge per cubic cm) at some point between the electrodes,  $V$  the potential at that point, then by Poisson's equation

$$\frac{d^2V}{dx^2} = 4\pi\rho.$$

Also the current  $i$  per sq. cm. at right angles to the direction



of the field is clearly equal to the charge per unit volume into the velocity,  $v$ , with which the charges move, i.e.

$$i = \rho v,$$

where  $v$  is given by the equation

$$\frac{1}{2}mv^2 = Ve$$

Hence

$$\frac{d^2V}{dx^2} = 4\pi i \sqrt{\frac{m}{2Ve}}.$$

Now if we neglect the small intrinsic velocities with which the electrons are emitted from a hot cathode (usually a small fraction of a volt), we have seen that the maximum current will be attained when the field at the surface of the cathode has been reduced to zero by the space charge effect. Hence for the maximum current we have  $dV/dx = 0$  when  $x = 0$ , if we measure our distances from the surface of the cathode, and integrating our equation with this condition we have

$$\left(\frac{dV}{dx}\right)^2 = 8\pi i \sqrt{\frac{2Vm}{e}}$$

Integrating again, and remembering that  $V$  is zero when  $x$  is zero, i.e. at the surface of the cathode, we have finally

$$i = \frac{\sqrt{2}}{9\pi} \sqrt{\frac{e}{m}} \frac{V^{3/2}}{d^2}.$$

If  $i$  and  $V$  are measured and the distance apart of the plates is known this equation can be used to determine the ratio  $e/m$  for the thermionic carriers. This experiment has actually been carried out<sup>(6)</sup>, the result obtained being  $1.76 \times 10^{17}$ , a very satisfactory agreement.

If, now, the cathode is maintained at a constant high temperature, and the potential difference is gradually increased, the current at each point will be the maximum current for the given potential until the latter is raised to such a point that the current becomes the saturation current for the given temperature. The saturation current is given by Richardson's law, and will depend only on the temperature. We have so far supposed that the electrons are emitted without any intrinsic velocity. As a matter of fact, as we have seen in section 65, they are given out with varying velocities distributed according to Maxwell's law

Thus it will require a reversed potential to stop the emission completely, the emission becoming smaller as the reversed potential rises according to some law which can be deduced from the distribution of velocities among the emergent electrons. The complete curve between the current and potential for a thermionic valve thus consists of three parts (1) an initial portion governed as just described by Maxwell's distribution law, (2) an intermediate portion governed by the space charge and obeying Langmuir's law, and (3) the final or horizontal portion, where the current corresponds to the saturation current for the temperature of the cathode. These conclusions have been verified experimentally, and a typical curve is shown in Fig. 52. The discussion of the application of these curves to triode valves is outside the purpose of this volume.

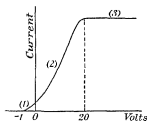


Fig. 52

**69 Conductivity of flames** If two platinum plates are placed a centimetre or so apart in a wide Bunsen flame and one of them is raised to a moderately high potential by means of a cabinet of small accumulators a current passes between the plates through the flame which is generally sufficiently high to be measured by an ordinary galvanometer if one of the terminals of the instrument is connected to the insulated plate and the other to earth. The current between the plates increases as the potential difference is increased in the manner indicated in Fig. 53. The curve in some respects resembled the curve for an ionized gas (Fig. 6). The current, however, showed no appearance of saturation. Even when the field applied rose as high as 300 volts per cm. increasing the field still produced an appreciable increase in the current. The curve in fact approximated very closely to a parabola, and the relation between the current  $i$  and the potential difference  $V$  was expressed by an equation of the form

$$i^2 = A V \dots \dots \dots (60)$$

where  $A$  is a constant.

The variation of the current with the distance between the

electrodes also differs markedly from the saturation current through an ordinary gas. In the latter case the current for a given field is proportional to the distance between the electrodes, in the case of the current through the flame it is independent of the distance between the electrodes providing that they both remain within the flame.

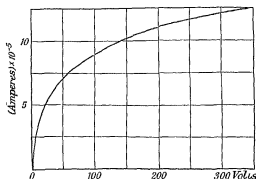


Fig. 53

**70 Distribution of potential between two electrodes in a flame** The origin of these differences is made clear when the distribution of potential across the flame is examined. This can readily be done as in the case of the discharge tube (§ 41) by means of a fine platinum exploring wire, connected to one of the quadrants of an electrometer. The wire being in the presence of positive and negative ions takes up the potential of the point in which it is placed. If two such wires are placed at a fixed distance apart and connected to adjacent quadrants of the electrometer, the deflection of the electrometer (which is proportional to the difference of potential between the two wires) will be a measure of the actual field at the part of the flame under observation.

Fig. 54 shows the potential at different points between two electrodes placed 18 cm. apart in a flame and maintained at a potential difference of 580 volts. The abscissae give the distance of the exploring wire from the positive electrode, the ordinates the difference of potential between the exploring wire and the negative plate. It will be noticed that the potential

ises very rapidly near the negative plate, no less than four-fifths of the total change of potential taking place within the first two centimetres from the cathode. The potential then rises slowly but uniformly until the neighbourhood of the anode is reached when a further sharp rise takes place<sup>(9)</sup>.

The field is, therefore, very intense near the cathode and very weak but uniform across the rest of the gas, except for a slight rise near the anode. The actual field in the greater part of the flame therefore never approaches saturation value in spite of the large average value of the field between the electrodes.

The problem, which is essentially similar to that of the

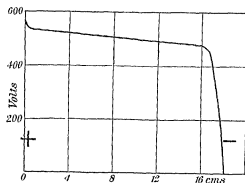


Fig. 51

current through a thermionic valve, can be investigated theoretically as follows.

Let  $n_1$  be the number of positive ions per c.c. at any point,  $e_1$  their charge and  $k_1$  their mobility, while  $n_2$ ,  $e_2$  and  $k_2$  denote the corresponding values for the negative ions. The current per sq. cm. at the point is thus equal to  $n_1 e_1 k_1 X + n_2 e_2 k_2 X$  where  $X$  is the value of the electric field at the point. In general the ions in gases all carry the same charge  $e$ , in which case we may write, the current

$$i = Xe (n_1 k_1 + n_2 k_2) \quad (61)$$

Now if there is no accumulation of ions at any point the field will be constant across the gas. If, however, there is an excess, say, of positive ions this will produce a space charge in the

gas equal to the excess of positive over negative, that is to  $e(n_1 - n_2)$  per unit volume. By the ordinary laws of electrostatics we have therefore

$$\begin{aligned}\frac{dX}{dx} &= 4\pi \times (\text{space charge}) \\ &= 4\pi e (n_1 - n_2). \quad \dots \quad (62)\end{aligned}$$

In the part of the gas where the field is constant  $dX/dx = 0$ , and thus  $n_1 = n_2$  or the number of positive and negative ions are equal.

Now when the gas has reached a steady state the number of positive and negative ions in each unit of volume must remain constant. Hence considering unit of volume at a distance  $x$  from one of the electrodes the excess of the number of ions leaving the volume over the number entering it owing to the action of the field must be equal to the rate of formation of the ions in the unit volume less the number lost by recombination. Now the number flowing out over one face perpendicular to the current, and therefore parallel to  $x$ , less the number flowing

in at the other face is equal to  $\frac{d}{dx}(n_1 k_1 X)$  for the positive ions, and  $-\frac{d}{dx}(n_2 k_2 X)$  for the negative ions. Each of these quantities must by the above be equal to  $q - \alpha n_1 n_2$  where  $q$  is the rate of formation of the ions and  $\alpha$  the coefficient of recombination (§ 11). Thus we have

$$\left. \begin{aligned}\frac{d}{dx}(n_1 k_1 X) &= q - \alpha n_1 n_2 \\ -\frac{d}{dx}(n_2 k_2 X) &= q - \alpha n_1 n_2\end{aligned}\right\} \quad \dots \quad (63)$$

Combining these equations with (62) and solving, we have, if  $k_1$  and  $k_2$  are constants for all parts of the field,

$$\frac{d^2 X^2}{dx^2} = 8\pi e (q - \alpha n_1 n_2) \left( \frac{1}{k_1} + \frac{1}{k_2} \right). \quad \dots \quad (64)$$

Now in the part of the field where the potential gradient is constant the field is constant and hence  $dX/dx$  is zero, and thus  $d^2 X^2/dx^2$  is also zero. Hence for this part of the field

$$q - \alpha n_1 n_2 = 0, \quad \dots \quad (65)$$

that is to say, the recombination exactly balances the ionization. Thus the ions formed in this layer all recombine there, none of them reaching either electrode. In other words the ionization in this part of the gas contributes nothing to the current, which is, therefore, independent both of the extent and also of the intensity of ionization in this layer. Hence so long as there is any portion of the gas in which the field is uniform the current will be independent of the distance apart of the electrodes.

On the other hand in the neighbourhood of either of the electrodes the recombination will be small. Taking the case of the cathode, for example, the negative ions are flowing rapidly away from the cathode while the positive ions are flowing in. Hence close to the electrode itself there will only be positive ions present and recombination cannot occur. Thus  $\frac{d^2X^2}{dx^2}$  will increase rapidly as the electrode is approached and hence there will be a rapid rise in the field at this point in the gas. Similar considerations apply to the positive electrode.

It has been shewn by Sir J. J. Thomson that the fall of potential in the layer near the cathode is proportional to the square of the current passing through it. The fall of potential in the uniform field has been shewn to be directly proportional to the current. The total fall of potential  $V$  between the electrodes should thus be given by

$$V = A i + B i^2 \quad (66)$$

If  $A$  is small compared with  $B$  this reduces to  $V = B i^2$ , an expression which as we have seen represents closely the experimental results.

The above analysis applies to all cases of gaseous conduction where the applied difference of potential is less than the saturation voltage. As, however, saturation voltages are generally employed wherever possible, it has no practical application except in the case of flames.

**71 Conductivity of salt vapours.** The presence of salts in the Bunsen flame greatly increases its conductivity especially if the salts are those of the alkali metals. The increase in the

current is, however, only appreciable if the salt vapour comes in contact with the cathode. We have seen that the ions formed in the middle part of the flame add nothing to the current and hence increasing the number of ions there has no effect. If, however, we increase the conductivity of the layer near the cathode in which practically the whole fall of potential takes place, the current will rise very rapidly and may often be several thousand times greater than the current for the same potential difference in the unsalted flame.

Since the fall of potential near the anode is small compared with that near the cathode the increase in the current due to salting the flame near the anode is comparatively small. Hence if one of the electrodes is coated with salt and an alternating electromotive force applied to the electrodes a very large current will pass when the coated electrode is negative and only a very small one while it is positive. An arrangement of this kind practically lets current through in one direction only, and might thus be used as a rectifier.

**72. Maximum current carried by salt vapours** The current in salted flames is carried by the atoms of the radicals in the compound in the same way as the current in electrolytic solution. The matter has been investigated quantitatively by H. A. Wilson. A current of air was passed down a metal tube with a central wire electrode the whole being heated to a bright red heat in a furnace. If salt was added by spraying salt solution into the air current, a considerable current passed between the electrodes. This current was found to be exactly the same as that passing through a solution of the same salt in water when the rate at which the salt was being decomposed in solution was made equal to the rate at which salt was being supplied to the tube. The carriers of the current are thus the same in each case and carry the same charge.

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## CHAPTER IX

### PHOTO-ELECTRICITY

73    **The photo-electric effect.** For some years before the development of the ionization theory gave an explanation of the effect it was known that a metal plate when illuminated by light from an arc or spark discharge emitted negative electricity. In general if the plate was carefully insulated it was found to acquire a small positive charge and hence a small positive potential, which however never exceeded about one volt. After this potential was reached the emission of electricity ceased. In most cases the effect was completely stopped if a sheet of glass was interposed between the light and the metallic plate, and it was thus shewn to be due to the ultra-violet portions of the spectrum. The alkali metals were, however, peculiarly sensitive and responded to rays from the luminous part of the spectrum even as far as the red. They could thus be excited by the light from a candle.

Whatever the nature of the surrounding medium or the state of the metallic surface the phenomenon was to be observed, but the rate at which electricity was emitted was found to be exceedingly variable, depending on the pressure and nature of the gas around the plate, the state of polish of the surface and even on the length of time since the plate was last polished. The effect is known as the *photo-electric effect*, or occasionally as the Hallwachs effect after one of its earliest investigators.

We now know that the effect is due to the emission of slowly moving negative electrons. They are often spoken of as *photo-electrons* to indicate their mode of production, but there is nothing except their speed to distinguish them from the electrons which make up the cathode rays. By enclosing the illuminated plate in a high vacuum, the ratio of the mass to the charge can be measured for the photo-electrons most conveniently by

the use of the relations (42), (43), § 47 The ratio is found to be the same as for the cathode ray particles, that is to say, the negative emission takes the form of electrons. The effect is, in fact, a form of ionization The light incident on the metal ionizes the atom of the metal, causing the emission of a negative electron with some small velocity, the atom itself being left with a positive charge. If the electron is ejected near the surface of the metal it will escape carrying away its negative charge. The process is thus identical with ordinary ionization except that the positive ion being in a solid is not free to move, and the whole current is carried by the negative ions

This identity was at first concealed by the fact that ultra-violet light was not known to produce ionization in gases Gases are, however, now known to be capable of ionization by light if light of suitable wave length is employed

It has been found that for every substance there is a definite wave length at which the photo-electric emission commences, rays of longer wave length than the critical value producing no effect This maximum wave length is greater according as the element is more electro-positive and shorter as the element becomes more electro-negative Thus for the alkali metals which are extremely electro-positive, the critical or maximum wave length which will excite photo-electricity is actually in the visible spectrum being greater for caesium than for potassium and sodium, for other metals the critical wave length lies between  $4000 \times 10^{-8}$  and  $2500 \times 10^{-8}$  cm For the non-metals waves of still shorter wave length are necessary to produce the effect. oxygen, for example, only emits photo-electrons if the incident rays have a wave length not greater than  $1350 \times 10^{-8}$  cm

Now light of this wave length is exceedingly absorbable in almost all kinds of matter It is completely absorbed by quartz, but is transmitted by an exceptionally good crystal of fluor-spar The early attempts to ionize gases by light failed because the wave length of the radiation employed was too great.

**74. Ionization of gases by ultra-violet light.** Owing to their much smaller density and the difficulty of obtaining light of sufficiently short wave length, the effect in gases is

very much smaller than that at the surface of a metal, and the greatest care has to be exercised to avoid spurious effects due to the reflection of some portion of the incident light on to the metal electrodes of the chamber used for measuring the effect. The only satisfactory method is to expose the gas to the light in one chamber and then to pass it through a narrow winding tube to a second chamber in which its ionization is tested, relying on the slowness with which the ions recombine to enable them to persist until they can be measured. A suitable form of apparatus used by Hughes (1) is shown in Fig. 55. The light is produced by a discharge in hydrogen in a discharge tube *T* of special shape, the hydrogen discharge being very rich in the extreme ultra-violet. The gas under investigation

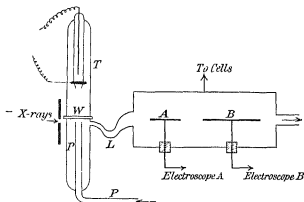


Fig. 55

is passed through the tube *P* and emerges close to a window *W* of exceptionally transparent fluor-spar, where it is ionized by the rays transmitted. It then flows through the winding tube *L* to the ionization chamber. If any ions are formed in the gas, a current passes between the outer wall which is connected to a battery of cells and the electrode *A*. The second electrode *B* enables an estimate to be made of the coefficient of recombination of the ions formed. Keeping the apparatus the same but replacing the light by X-rays it can be shown by direct comparison that the ions have the same coefficient of recombination in the two cases, and are thus presumably of the same nature.

The hydrogen discharge gives radiation of wave lengths from 1300 to 1600. Thin quartz becomes transparent for rays of wave length about 1450. If the fluor window  $W$  is replaced by quartz no ionization is produced in air. Hence the maximum wave length for air is somewhere between 1300 and 1450, or roughly 1350 as stated above. In chlorine which is still more electro-negative all attempts to produce ionization by light have so far failed. Various compound gases such as carbon dioxide and ammonia are ionized by the light coming through a thin quartz window, that is their maximum wave length is greater than  $1450 \times 10^{-8}$  cm.

75. Velocity of emission of the photo-electrons. It is found that a plate illuminated by ultra-violet light gives electrons of all velocities from a certain maximum downwards. The velocity is most conveniently measured by measuring the difference of potential necessary to prevent the escape of electrons from the plate. Suppose the metal plate emitting the electrons is at a positive potential  $V$ . The negative electron will experience a force attracting it backwards to the plate and by the time it reaches a place of zero potential it will have lost a quantity of energy equal to  $Ve$ , where  $e$  is its charge. If the original energy with which it left the plate was  $E$  it will now have energy equal to  $E - Ve$ . If this is equal to zero it will just escape being dragged back to the plate. Obviously if its initial energy is less than  $Ve$  its motion will be reversed and it will return to the plate again. Thus the minimum velocity an electron can have to escape is given by

$$\frac{1}{2}mv^2 = Ve,$$

$$v^2 = 2V \frac{e}{m}.$$

If the active plate is surrounded by conductors at zero potential and carefully insulated it will gradually acquire a positive potential owing to loss of negative electricity. This potential will grow until it is just sufficient to prevent the escape of the fastest electrons which the plate emits. Thus a measurement of the potential acquired by a plate exposed under these circum-

stances to ultra-violet light will enable us to estimate the velocity of the swiftest electrons emitted.

On this account the very objectionable practice has grown up of stating the velocity in terms of the voltage acquired by the plate, and thus phrases like "a velocity of one volt" have become common. As will be seen from the formula the velocity is not even proportional to the potential but to the square root of it. The real velocity can readily be calculated from the formula, since  $e/m$  is equal to  $1.77 \times 10^7$  e.m.u. Thus a "velocity of one volt" or  $10^8$  e.m.u. is equal to about  $5.9 \times 10^7$  cm./sec.

Experiments have shewn that the velocity with which electrons are emitted is independent of the intensity of the light. The energy imparted to the individual electron is thus independent of the energy of the exciting radiation, a remarkable result which was first recorded by Lenard. For a given substance the velocity of the electrons emitted is a function of the frequency of the incident radiation. It is found, in fact, that for a given substance the maximum potential acquired under the action of light of frequency  $\nu$  can be expressed by the linear relation

$$V = h\nu - V_0, \quad (67)$$

where  $V_0$  is a constant which varies with the substance employed but  $h$  has exactly the same value for all substances.

The most rigorous proof of this law has been provided by Millikan (2). In order to employ as wide a range of frequencies as possible he worked with the alkali metals for which the photo-electric effect begins in the visible spectrum, and his observations extended over a range of frequencies of nearly three octaves. The experiments were carried out in an exceedingly high vacuum, and in order to obtain really clean surfaces, the surfaces were actually turned up in the vacuum itself, by means of a tool which could be operated from outside by an electromagnet. Not the slightest deviation from the linear law was observed, and the value of  $h$  was found to be  $4.128 \times 10^{-15}$  to an accuracy of at least 1 per cent.

The significance of the experimental relation (67) can be made clear by multiplying the equation throughout by the electronic charge  $e$ , and transposing. Thus

$$Ve + V_0e = h e \nu. \quad (68)$$

Now  $V_e$  is the energy with which the fastest electron escapes from the illuminated surface.  $V_0$  has also the dimensions of energy and can only be interpreted as measuring the work done by the electron in escaping from the solid, that is to say the work done by the electron in escaping from the surface together with the work done, if any, in escaping from the parent atom. Millikan's latest experiments (3) have led him to the conclusion that the latter is zero in the case of a metal, and that  $V_0$  measures the contact P.D. between the metal and its surroundings. Thus  $V_e$  measures the energy with which the electron escapes,  $V_0$  the energy used in the process of escaping, and thus the left-hand of equation (68) is the total energy with which the electron starts its career. Thus if monochromatic light of frequency  $\nu$  falls upon any substance the initial velocity imparted to the electrons is given by the relation

$$\frac{1}{2}mv^2 = h\nu, \quad (69)$$

where  $h$  is a constant which is independent of the nature of the substance, and is equal to  $ke$ . Taking Millikan's value for  $k$  and converting volts to electrostatic units, we have

$$h = 4.774 \times 10^{-10} \times \frac{4.128 \times 10^{-16}}{300} = 6.56 \times 10^{-27} \text{ ergs sec}$$

It will be seen that equation (69) is merely an expression of well-ascertained experimental facts.

**76 The quantum theory.** In order to explain the laws governing the thermal radiation from a perfect radiator Planck had been led to formulate the hypothesis that an accelerated electron did not radiate energy continuously, as demanded by the classical electromagnetic theory of light (see § 84), but only intermittently, each emission consisting of a definite burst or *quantum* of energy (4). The energy in one of these quanta was supposed to be directly proportional to the frequency of the radiation emitted. Thus if  $\nu$  is the frequency of the radiation the energy associated with each quantum of it is given by

$$w = h\nu, \quad (70)$$

where  $h$  is a universal constant, known as Planck's constant. The value deduced for this constant was

$$h = 6.55 \times 10^{-27} \text{ ergs sec}$$

It is therefore identical with the  $h$  of the previous section

We can illustrate Planck's law quite readily from phenomena which we have already considered. We have seen (§ 3.3) that an electron may be transferred from its normal position in the atom to some other condition of greater energy by the impact upon it of another electron if the latter has a certain minimum energy, measured by  $Ve$ , where  $V$  is the resonance potential for the atom. This minimum energy is clearly the difference in energy of the atomic electron in its two conditions. Thus the potential energy of the electron in its abnormal condition will be  $Ve$  units greater than in its normal state, and  $Ve$  units of energy will be set free when the electron falls back into its stable condition (5). This energy, as we mentioned, is radiated as monochromatic light of definite frequency, only one line appearing in the spectrum. The frequency of this radiation, by Planck's law, should be given by the relation

$$w = Ve = h\nu, \text{ or } \nu = Ve/h$$

If we take the case of mercury vapour there is a resonance potential  $V$  at about 1.8 volts or  $1.6 \times 10^{-2}$  e.s.u. and the radiation emitted should thus be given by

$$\nu = \frac{1.6 \times 10^{-2} \times 4.774 \times 10^{-10}}{6.55 \times 10^{-27}} = 1.15 \times 10^{15}$$

The frequency of the light actually emitted is  $1.18 \times 10^{15}$ . The agreement is perfect, considering the possible errors of the measurement of resonance potentials.

In Planck's original form of the theory only the emission occurred in quanta, the atom or electron being supposed to absorb radiation continuously until its energy reached that of the quantum for the radiation concerned. In 1905 Einstein (6) made the further assumption that the radiation actually travelled in minute bundles each possessing the quantum corresponding to its frequency, and that the atom or electron absorbed either the whole of this quantum or none at all. This assumption leads immediately to our experimental relation (69). From monochromatic light of frequency  $\nu$  the atom will absorb a whole quantum of energy  $h\nu$ , and this energy when transferred to an electron will give it kinetic energy  $\frac{1}{2}mv^2 = h\nu$ . At the time

the data for testing this equation did not exist, and the suggestion was not well received, as the idea of a definite quantum of radiation travelling through space as an entity appeared to be completely irreconcilable with the wave theory of light (1)

So drastic an assumption is not absolutely necessitated by the results of § 75. It is possible to conceive that the atom absorbs energy from the radiation continuously until the quantum is reached and then ejects this superfluous energy in the form of a photo-electron. This mode of escape is, however, made impossible by the following considerations. However weak the incident light may be the emission of photo-electricity commences as soon as the light falls on the surface. There is no lag, or incubation period, in the effect. Now the photo-electric effect for sodium can easily be detected with an ordinary candle at a distance of 3 metres. This corresponds to an energy of 1 erg per sq. cm. per sec. falling on the surface of the metal, and of this not more than one-third is of sufficiently short wave length to excite the photo-electric effect. Now the area of cross section of an atom is of the order of  $10^{-15}$  sq. cm. and the maximum energy which could be absorbed by the atom from the beam, if uniform, would be therefore about  $\frac{1}{3} \times 10^{-15}$  ergs per sec. But the energy of the electrons emitted is of the order of  $5 \times 10^{-13}$  ergs. To accumulate this energy the atom would have to go on absorbing for about 15,000 seconds or more than four hours. The suggestion of a gradual absorption from a uniform beam is therefore inconsistent with the facts, and we are driven back on Einstein's assumption.

If the quantum of energy of the incident radiation is less than the energy  $V_0e$  required to extract an electron from the substance, the atom which can only absorb by quanta will not attain sufficient energy to eject an electron, and the photo-electric effect will cease. The smallest frequency  $\nu$  for which photo-electrons can be ejected is thus given by  $V_0e/h$ . The longest wave length which can excite the effect is  $c/\nu$ , where  $c$  is the velocity of light. This is different for different substances.

The quantum theory in reality is not a theory: no theoretical basis has yet been found for it. It is a fundamental law governing the exchange of energy between radiation and matter, and in all



cases in which it has been tested it is found to express the phenomena with great exactitude. We shall meet with further examples in the following chapter. The question as to how the quantum relation is to be reconciled with the electromagnetic theory of light, or in fact with any form of wave theory, is the most difficult and interesting problem in modern physics.

### 77. Distribution of velocities among the photo-electrons

So far we have considered only the maximum velocity of the electrons which emerge from the metal. If we maintain a constant difference of potential  $V$  between the radiator and its surroundings less than the maximum positive potential which would be acquired by the plate, the rate of loss of electricity from the plate, that is, the negative current from it, will be proportional to the number of electrons which leave the plate with an energy greater than  $Ve$ , the energy which would be required to escape from the positively charged plate. In this way the proportion of the electrons which emerge with various velocities less than the maximum can be measured.

On making the experiments it is found that the electrons emerge with all velocities from zero up to the maximum. It need not be assumed (and is indeed very improbable) that they are actually ejected from the atom with different velocities. The electrons will be formed at different depths in the metal (since the light can penetrate small thicknesses of metal) and hence will have different thicknesses of metal to traverse before escaping from the surface. Now in passing through matter electrons lose velocity owing to collisions with the molecules. Thus these electrons which are formed at the surface, having no matter to traverse, will escape with the actual velocity with which they left the atom. Those formed deeper in the metal will lose some of their velocity before reaching the surface, until at last a layer is reached the electrons from which will be unable to penetrate to the surface at all.

**78. Magnitude of the photo-electric effect.** *The magnitude of the photo-electric effect may be defined as the total current from unit area of the illuminated surface when its potential*

is favourable to the escape of negative electricity. Except under very special conditions it is an exceedingly variable quantity, and many futile experiments have been made on it. In the presence of gas it is found to depend on the pressure of the gas in a very complicated way. All surfaces condense on themselves a surface layer of gas or vapour which is exceedingly difficult to remove even in a vacuum. This layer may also be electrically charged and so influence the escape of the photo-electrons not only by its absorption but also by its field. Consistent results can only be obtained with films or surfaces not only kept but also prepared in the highest vacua obtainable and never exposed at any period to the action of a gas at a perceptible pressure. This applies also but to a smaller extent to experiments on the velocity of the electrons, especially if the layer is charged. Velocities as much as six or seven times the normal maximum for the metal have been observed for example in the case of a radiator which has been used as the cathode in a discharge tube.

An apparatus (7) suitable for the preparation and investigation of a metallic surface in vacuo is shewn in Fig. 56. The thick lines represent the metallic part of the apparatus which extends far enough on all sides to screen the plate  $P$  from external electrostatic effects. When in the position shewn the plate makes metallic contact with a Wilson electroscope  $E$ , while the two potentiometers  $V$ ,  $V$  can be adjusted so as to maintain a constant measured difference of potential between the radiator and its surroundings. To obtain a film on the radiator  $P$  it is lowered to the position  $P'$  opposite the mouth of a small quartz crucible  $F$ , which contains the metal under investigation and can be electrically heated by the wires  $w$ ,  $w$  passing through the walls of the tube. The metallic vapours condense on the cold plate forming a film which, as the whole apparatus is maintained at a high vacuum, has never been in contact with gas and so is free from the disturbing surface layer. If the outer case is earthed the maximum potential acquired by the plate  $P$  as measured by the electroscope gives the maximum velocity of emission of the photo-electrons, as already explained. By applying a small accelerating potential

sufficient to produce the maximum emission the total photo-electric effect can be measured

With films prepared and kept in vacuo, the total photo-electric effect is found to be directly proportional to the intensity of the light for intensities varying in a ratio of as much as 1 to  $10^6$ . On account of its importance with respect to the quantum theory of radiation experiments with exceed-

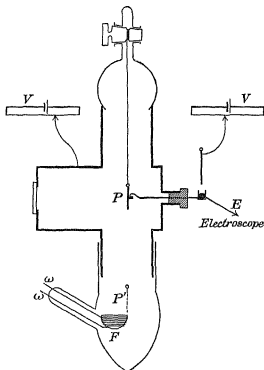


Fig. 56

ingly small intensities of illumination have been made, but even when the energy was as small as  $10^{-7}$  eigs per sq cm per sec no departure could be observed from the proportionality between the intensity and the current. The current is also independent of whether the light is continuous or is given out in a series of brief flashes. As long as the average energy remains constant the emission remains the same

Temperature also is without influence on photo-electric emission on surfaces in vacuo although it has a considerable effect on surfaces in air, probably owing to changes in the layer of condensed gas

**79. Variation of the photo-electric effect with wave length and state of polarization.** For the majority of metals the photo-electric effect increases as the wave length of the exciting radiation diminishes. The alkali metals for a certain part of the spectrum and with oblique incidence of the light form an exception, the current rising to a fairly sharp maximum at a definite wave length. In these metals the effect also depends on the plane of polarization of the incident light.

Let light be incident obliquely on a surface, say, of liquid alloy of sodium and potassium. These liquid alloys are convenient since they give perfectly plane surfaces. The plane containing the ray and the normal to the surface is known as the plane of incidence. According to the electromagnetic theory of light, if the light is plane polarized in the plane of incidence the electric field in the pulse will be perpendicular to this plane, that is, parallel to the surface of the radiator. We will denote this state as the  $E_{\parallel}$  plane to indicate that the electric force is parallel to the radiating surface. On the other hand, if the light is plane polarized at right angles to the plane of incidence the electric field will be parallel to the plane of incidence and thus will have a component if the ray is oblique, perpendicular to the surface. The more oblique the incidence the greater this component. We will denote this state of polarization by  $E_{\perp}$ .

If now experimental curves are drawn between the photo-electric intensity and the wave length of the incident light for the two states of plane polarization the results shown in Fig. 57 are obtained. It will be seen that when the electric field in the light waves is parallel to the surface of the radiator the emission decreases uniformly as the wave length is increased. When, however, the light is polarized so that the electric field in the radiation has a component perpendicular to the radiator, the emission rises rapidly as the wave length decreases, reaches a maximum for a certain definite wave length and then decreases

until it joins the other curve. The maximum intensity increases with the obliquity of the rays, but the corresponding wave length is constant. The ratio of the maximum to the normal effect differs widely for different surfaces even of the same alloy. It is normally as much as 15 to 1, but has been observed as high as 300 to 1, with an angle of incidence of  $60^\circ$ . The velocity of the electrons emitted is the same in the two cases.

So far as is yet known this selective effect is confined to the alkali and alkali earth metals and is only apparent over a comparatively short part of the spectrum. In the diagram (Fig. 57) which represents the case of a sodium-potassium

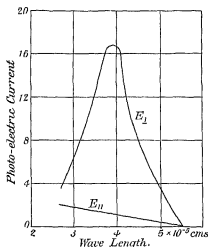


Fig. 57

alloy the maximum effect is reached at a wave length of  $3400 \times 10^{-8} \text{ cm}$ , for potassium the corresponding wave length is 4490 and for rubidium about 5000, that is, in the yellow green of the visible spectrum. The curve obtained with unpolarized light may obviously be obtained by compounding the two separate curves. If the light is incident normally on the surface the effect, of course, disappears, since the light has then no component normal to the surface.

The photo-electric effect is of considerable magnitude, especially in the case of the alkali metals which as we have seen

have their maximum efficiency in the visible spectrum. The current produced can be largely increased by making use of ionization by collision, in the surrounding gas. Rubidium cells containing some inert gas such as argon at a pressure, chosen so as to produce the maximum amount of ionization by collision, have been used as radiometers to measure small quantities of radiation. Such a cell will easily detect the light radiation from a single candle at a distance of three miles, and is thus not at all inferior in its powers to the human eye.

**80. Photo-electric fatigue** If a plate is polished and tested at various intervals, it is found that its photo-electric efficiency decreases. Thus the current from a polished copper plate falls to one-third of its initial value if exposed to the air of a room for a single day. If on the other hand it is kept in a closed vessel containing air at the atmospheric pressure, the same amount of fatigue takes three months to develop. The effect doubtless has to do with the surface layer of gas condensed on the metal. Careful experiment has shown that it does not occur with perfectly gas free surfaces kept in high vacua. The effect has been ascribed to ozone, to hydrogen peroxide, and to other gases, but the observations of different experimenters are exceedingly discordant.

**81. Photo-electric effect in non-metals** The photo-electric effect can also be detected in non-metals, but owing to their more electro-negative character the maximum wave length at which the effect commences is smaller than in the case of metals. For carbon, for example, the emission of electrons begins when the wave length is reduced to 2550. The observations are somewhat more difficult to make if as usually happens the non-metal is also a non-conductor. In this case the charge on the surface is not conducted to a wire leading to the electrometer, and the positive charge accumulates until its potential is sufficient to stop the emissions of the photo-electrons. The accumulated charge can be measured by transferring the substance bodily into a Faraday cylinder connected with an electrometer. The charge measured by the electrometer is by the

ordinary laws of electrostatics equal to that on the substance. The emission of electrons takes place throughout the mass of the substance as far as the light penetrates it. Owing to the presence of these free electrons in the substance a certain conductivity is imparted to those layers of it which actually come under the action of the light which lasts so long as the illumination is continued. Thus if a sheet of sulphur is enclosed between two electrodes and illuminated by the light from a quartz mercury lamp a current passes which increases uniformly with the voltage between the two electrodes. The conductivity is independent of the applied field up to 400 volts per mm. With a field of this intensity currents of the order of  $2 \times 10^{-9}$  amps were observed when the sulphur was illuminated.

**82 Phosphorescence and the photo-electric effect** No connection can be traced between photo-electricity and fluorescence, many fluorescent compounds being quite inactive. On the other hand, phosphorescent substances always shew a well-marked photo-electric effect. Thus calcium sulphide with a trace of powdered bismuth and a flux of sodium borate yields a very actively phosphorescent substance. On testing this it was found to be exceedingly photo-electric also, giving a photo-electric effect nearly as large as brightly polished magnesium. The three substances taken separately and also in pairs were found to be neither phosphorescent nor markedly photo-electric. By using absorbing screens it could also be shewn that light which did not produce phosphorescence did not produce a photo-electric effect. The two effects, therefore, seemed to run parallel to each other.

It has been shewn that phosphorescence is due to certain active centres in the "phosphor." In all probability these centres under the action of light emit an electron which if the centre is sufficiently near the surface escapes as a photo-electron. If the centre is too deep for this the electron remains embedded in the substance, which is always a non-conductor. Eventually, however, under the action of the attraction of the now positively charged centre the electron finds its way back into the "centre," producing disturbances there which cause the emission of the

phosphorescent light. The photo-electric effect is thus connected with the excitation of phosphorescence, and not with the phosphorescence itself. The photo-electric effect itself ceases as soon as the exciting radiation is cut off.

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## CHAPTER X

### X-RAYS

83 **Production of X-rays.** It was discovered by Rontgen in 1895 that if a discharge tube at low pressure was worked in the neighbourhood of a fluorescent screen the latter became illuminated as if exposed to ordinary light, and photographic plates were also affected, even though protected in their usual wrapping of opaque black paper. These effects were found to have their origin in radiations proceeding from those portions of the walls of the discharge tube struck by the cathode rays. These radiations pending a further inquiry into their nature were called X-rays. They have also been called Rontgen rays, after

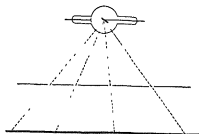


Fig 58

their discoverer. The former term, however, seems to have found more favour, and is now almost universally employed.

The fact that the photographic plates are affected through the black paper shews that the rays can traverse substances opaque to ordinary light. Their penetrating power indeed depends principally upon density, light substances like paper, flesh, wood, etc., being relatively transparent to the rays, while dense ones such as bone, and most of the metals, being comparatively opaque. Thus, if a hand is placed between the source of the X-rays and a fluorescent screen the shadows

cast by the relatively opaque bones are distinctly visible, a result which has given these rays their great importance in surgery

The shadows cast by the rays coming from the walls of an ordinary discharge tube are naturally blurred owing to the finite area of cross section of the cathode beam. If, however, we focus the cathode rays on to a single point by making use of a concave cathode a point source of X-rays is obtained and sharp shadows are cast. By joining points on the shadow to corresponding points on the obstacle (Fig. 58) and producing the lines backward they are found to meet in the spot where the cathode rays meet the walls of the tube, thus shewing that the X-rays start from the point struck by the cathode rays and travel out from it in all directions in straight lines

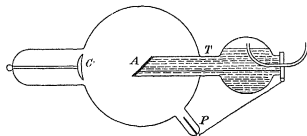


Fig. 59

Owing to the large amount of energy conveyed by the cathode rays it is impossible to focus them on the walls of the tube, the heat generated at the focus being sufficient to fuse glass in a few seconds. To overcome this difficulty the cathode rays are focused on a platinum or better still a tungsten plate supported in the centre of the discharge tube, and known as the anti-cathode. Even so with the currents which it is now possible to pass through the discharge tube the anti-cathode rapidly becomes red hot, unless special devices are employed to cool it. Of these the most successful is that in which the anti-cathode is cooled by water. A modern X-ray tube of this kind is figured in Fig. 59.

The cathode *C* is concave, and of aluminium, and is placed

platinum which is fused on the end of the tube *T* which can be filled with water. A separate anode *P* is also placed in the tube, and is in metallic connection with the anti-cathode. The action of the separate anode is somewhat obscure, but it has been found in practice to improve the working of the tube. The tube is generally run by an induction coil or high tension transformer. In modern X-ray photography the vacuum of the bulb is adjusted so that it works with a difference of potential of about 100,000 volts and currents of from 3-5 milliamperes are usually employed in the tube. The production of heat in the bulb is therefore some 100 calories per second.

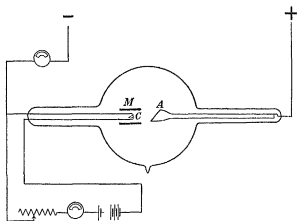


Fig. 60

We have seen that the potential required to send a discharge through a vacuum tube depends on the pressure of the residual gas, the smaller the pressure the higher is the required potential difference, and in consequence the greater the speed of the cathode rays. The quality of the X-rays produced depends on the velocity of the cathode rays. Thus a slight change in the pressure of the residual gas, which easily occurs when the tube is running, makes a considerable difference to the penetrating power of the rays. Also with the ordinary type of X-ray tube the penetrating power can only be altered by adjusting the vacuum. Devices for this are generally attached to the tube, but the adjustment requires some degree of experimental skill.

To avoid these difficulties a new type of tube, invented by Coolidge, has been placed on the market (Fig. 60). This tube is exhausted so completely of gas that no discharge can be sent across it when cold owing to the insufficient number of possible carriers left in the tube. To provide carriers for the discharge the cathode  $C$  is made of a spiral of tungsten wire which is heated to incandescence by means of an electric current. Large quantities of thermions are emitted, the number being a function of the temperature of the wire (§ 63). These thermions have very small velocities, but can be speeded up to any required extent by applying the corresponding P.D. across the tube. The velocity of the electrons and hence the quality of the X-rays emitted depends only on the P.D. applied across the tube. As the P.D. applied is always far above the "saturation" potential for the tube the current through the tube depends only on the temperature of the spiral. The tube is therefore completely under control.

The negative electrons can be focused into a beam by surrounding the wire with a tube of molybdenum,  $M$ . The anti-cathode  $A$  is made of a massive block of tungsten. No cooling device is usually necessary.

**84. Radiation emitted by the stoppage of a moving electrified particle. Classical Theory.** The fact that the X-rays have their origin at the point struck by the cathode rays led Sir G. Stokes to suggest that they are electromagnetic waves set up by the sudden stoppage of the rapidly moving electrons which make up the cathode stream. This view is now generally accepted.

The effect is most readily understood by a consideration of the Faraday tubes of force. If a charged cathode particle is moving with a speed which is small compared with that of light, its electric field will be the same as that for a particle at rest, and the tubes will be therefore distributed uniformly round the particle. Assigning all the effects in the field round the charge to the action of the Faraday tubes it can be shown that the motion of a single Faraday tube of force produces a magnetic field in the medium which is perpendicular to the length of the tube and to its direction of motion, and equal to  $4\pi v$ , where  $v$  is

the velocity of motion of the tube in a direction perpendicular to its length. (See J. J. Thomson, *Elements of Electricity and Magnetism*, Chap. XIII.)

Consider a single charged particle moving along a direction  $OX$  with a velocity  $v$ . This particle will carry with it a number of Faraday tubes of electric force, which when the motion has become steady will travel along as if rigidly attached to the particle.

Suppose the particle is suddenly stopped by striking a solid obstacle at the point  $A$  (Fig. 61), and let us suppose that disturbances are propagated along the Faraday tubes with a finite velocity  $c$ . It can be shown that this velocity is the velocity of light.

Let  $t$  be the time that has elapsed since the particle was stopped. Describe round  $A$  a sphere of radius  $ct$ . Then all the

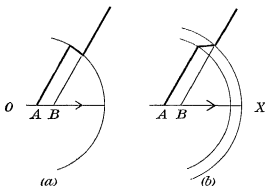


FIG. 61

portions of the tubes inside this sphere will be radiating from the stationary position of the particle at  $A$ . Outside this sphere however the disturbance produced in the Faraday tubes by the stoppage of the particle will not have arrived. They will thus be still moving in the direction  $OX$  with their original velocity  $v$ , and will be radiating from the position which the particle would have reached if it had not met the obstacle, that is, from a position  $B$  along  $Ox$  produced where  $AB$  is equal to  $vt$ .

There will thus be a relative displacement between the two

portions of the tube of force, and as we must regard the tube as continuous it is evident they must wrap themselves round the surface of the sphere

This sphere is expanding with a velocity  $c$ , and we thus have a sheet of electric force travelling out with a velocity  $c$  from the position of the particle. But the motion of the Faraday tubes at right angles to their length produces a magnetic field perpendicular to the Faraday tubes and to the direction in which they are moving, that is to say, also in the surface of the sphere. Thus a sheet of electromagnetic disturbance spreads out from the particle. This, on Stokes' theory, constitutes an X-ray.

It will not in general be possible to stop the particle abruptly. If  $\tau$  is the time taken to reduce the particle to rest, the disturbance will be enclosed by two spheres of radii  $ct$  and  $c(t + \tau)$  (Fig. 61 *b*). The thickness of the disturbance or pulse will thus be  $c\tau$  and will be smaller the more quickly the particle is stopped.

Let Fig. 61 *b* represent this state of affairs. Then, since  $AB = vt$ ,

$$\frac{\text{tangential electric polarization}}{\text{normal electric polarization}} = \frac{vt \sin \theta}{\delta},$$

where  $\delta$  is the thickness of the pulse and  $\theta$  is the angle between the direction of the tube and  $AX$ . But the normal polarization is  $e/4\pi r^2$  and thus since  $r = ct$  the tangential electric polarization

$$= \frac{e}{4\pi\delta} \frac{v \sin \theta}{c} \quad \dots \quad (71)$$

Now since this is moving at right angles to its direction with a velocity  $c$  it will produce a magnetic force  $H$ , equal to  $4\pi c$  times the polarization, that is

$$\frac{ev \sin \theta}{\delta} \quad \dots \quad (72)$$

Since these fall off inversely as the distance from the particle while the normal polarization falls off as the inverse square of the distance, the intensity in the pulse except for points near the particle will be great, compared with the intensity outside it. We shall thus get a pulse of electromagnetic disturbance travelling out from the particle, and behaving in many

respects like ordinary light. The chief differences are that in the first place the thickness of the pulse is found to be small compared with the wave length of visible light, while in the second place the X-rays lack that regular periodic character which occurs in a train of waves of constant wave length.

The energy in a pulse of this kind being equally divided between the electric and magnetic fields is equal to  $2 \times \frac{\mu H^2}{8\pi}$  per unit volume, i. e.

$$\frac{\mu e^2 v^2 \sin^2 \theta}{4\pi r^2 \delta^2}.$$

The energy radiated is thus zero along the direction of motion of the particle, and rises to a maximum at right angles to this direction. The volume of shell included between radii, making angles  $\theta$  and  $\theta + d\theta$  with the axis  $AB$ , is therefore  $\delta \cdot r \sin \theta \cdot 2\pi r d\theta$ , and the total energy in the shell is

$$\begin{aligned} 2 \int_0^{\frac{\pi}{2}} 2\pi r^2 \sin^2 \theta \delta \frac{\mu e^2 v^2 \sin^2 \theta}{4\pi r^2 \delta^2} d\theta \\ = \frac{2}{3} \frac{\mu e^2 v^2}{\delta} \end{aligned} \quad (73)$$

on substituting for  $H$  from (72) and evaluating the integral. The energy is thus inversely proportional to the thickness of the pulse. Thus the more suddenly the particle is stopped the greater the energy radiated.

The method can easily be extended to the case of the acceleration of a charged particle which is not actually brought to rest. If  $f$  is the acceleration then the time  $\tau$  which would be taken for the particle to be brought to rest is given by

$$v = f\tau.$$

Substituting this value for  $\tau$ , and the value  $c\tau$  for  $\delta$  in equations (71) and (72) we have

$$\text{Tangential polarization } D = \frac{ef \sin \theta}{4\pi r c^2}. \quad (74)$$

$$\text{Magnetic induction } H = \frac{ef \sin \theta}{rc}. \quad (75)$$

The flow of energy across unit area therefore (by Poynting's Theorem) is  $c^2 DH$

$$= \frac{e^2 f^2 \sin^2 \theta}{4\pi)^2 c} \quad . \quad . \quad (76)$$

Integrating over the area of the sphere of radius  $r$  we have

$$\text{rate of loss of energy} = \frac{2}{3} \frac{e^2 f^2}{c} \quad . \quad . \quad (77)$$

**85. The scattering of X-rays by matter.** Suppose the radiation from one electron falls upon another. The second electron while the pulse is passing over it will be subject to an electric field  $X$  and will thus have an acceleration

$$f_1 = X \frac{e}{m} = \frac{4\pi e D}{m} = \frac{e^2 f \sin \theta}{mrc^2}$$

substituting for  $D$  from (74). This electron will, therefore, give out radiation which, since  $f_1$  is proportional to  $f$ , will have the same quality as the radiation exciting it.

Thus if a beam of primary X-rays falls on a material substance, since all matter contains electrons, secondary X-rays will be given out in all directions which, since they are found to be of the same quality as the rays exciting them, have been called "*scattered radiation*," in order to distinguish them from another type of secondary radiation which may also be emitted the quality of which depends not on the primary radiation but on the chemical nature of the radiator. This latter type is often called "*characteristic*" radiation, since it is characteristic of the radiator used for the experiment.

These effects can easily be observed by allowing a narrow pencil of X-rays to fall on a thin sheet of aluminium, or paper. An electroscope placed near the radiator, but out of the direct line of the primary pencil, will lose its charge, shewing that ionizing radiations are being given out by the radiator. If the radiator is removed the rate of loss of charge becomes very small. If, however, a sensitive electroscope is employed it is possible to observe a residual effect due to the action of the primary pencil on the molecules of the air.

The scattered radiation is not uniformly distributed about the radiator. The simple theory already outlined leads to the conclusion that  $I_s$  the intensity of the radiation emerging from



the radiator at an angle  $\theta$  with the primary rays should be expressed in the form

$$I_{\theta} = I_{\frac{\pi}{2}} (1 + \cos^2 \theta) \quad . \quad . \quad (78)$$

where  $I_{\frac{\pi}{2}}$  is the scattered radiation emerging at right angles to the primary beam. The scattered radiation is thus a minimum in this direction, and approaches twice this value as the direction of the primary beam is approached.

Careful experiments have shown that this relation is not strictly true. In every case the intensity of the radiation on the side of the radiator from which the primary rays emerge is greater than that given out at a similar angle from the face by which the rays enter<sup>(1)</sup>. The distribution is thus unsymmetrical about a plane through the radiator at right angles to the primary beam. This is shown by the thick line curve in Fig. 62, which represents the author's results for the actual distribution of the scattered radiation around a thin aluminum radiator placed at  $R$ . The dotted line gives the theoretical distribution as determined by (78). The divergence is probably due to the disturbance produced by the neighbouring electrons in the atom on the path of the vibrating electron.

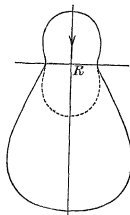


Fig. 62

**86 Polarization of the scattered radiation.** Consider a beam of cathode rays falling on an anti-cathode at  $O$  in the direction  $DO$  (Fig. 63). If the first impact of the electrons produced an X-ray the acceleration of the electrons would be in the direction  $OD$ , and the electric force in the resultant pulse at any point along the ray  $OP$  would be parallel to the plane of the paper. As a matter of fact the distribution of the primary rays round the anti-cathode shows that many of the cathode particles must experience considerable deviations owing to collisions with the electrons in the anti-cathode before producing a Röntgen ray, but at any rate we may expect a

preponderance of direct collisions and therefore a maximum electric force parallel to the plane of the paper. The effects will, therefore, be similar in kind but somewhat less in amount than in the simple case where all the electrons are stopped at the first collision. Since there is an excess of electric field in the pulses in a definite direction the emerging beam may be said to be polarized.

Suppose now that this partially polarized radiation falls on a mass of gas at  $P$ . The electric force will cause the electrons in the gas molecules to have an acceleration (§ 85), which if the beam is completely polarized will be in the direction  $PQ$  since the field must be in the plane of the paper and also perpendicular to the direction of the ray. Thus the electrons will be set vibrating in the direction  $PQ$ , and will emit radiation

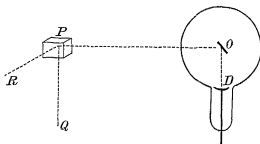


Fig. 63

which as we have seen will be zero in the direction of motion of the electron, and a maximum at right angles to it. Thus if the primary rays were completely polarized there would be no scattered radiation in the direction  $PQ$  while it would reach a maximum in a direction  $PR$  through  $P$  perpendicular to the plane containing  $OD$  and  $OP$ . In other words if we allow the rays from an X-ray tube to fall on a radiator we should expect that the scattered radiation would be a minimum in a line through the radiator parallel to the incident cathode rays, and a maximum in a direction at right angles to this. The experiments were carried out by Barkla (2) in 1904 and shewed a very marked effect, the polarization often reaching as much as 20 per cent. The actual amount depends on the hardness of the rays and the nature of the anti-cathode.

**87. Energy of the scattered radiation** The following expression has been deduced by Prof Sir J J Thomson for the energy of the scattered radiation. From (77) we have rate of loss of energy  $= \frac{2}{3} \frac{e^2 f^2}{c}$  where  $f$  is the acceleration produced in the radiating electron. The total energy given out when one complete pulse passes over the electron

$$= \frac{2}{3} \frac{e^2}{c} \int f^2 dt, \quad . \quad . \quad (79)$$

the integration extending throughout the time for which the pulse is acting on the electron. But  $f = \frac{Xe}{m}$  where  $X$  is the electric field in the primary pulse at any moment, and the energy radiated is therefore  $\frac{2}{3} \frac{e^4}{m^2 c} \int X^2 dt$ . We do not know the form of the X-ray pulse. If we assume that the field is constant throughout the thickness of the pulse and zero outside it,  $X$  is then constant during the time  $t$ . Also if  $\delta$  is the thickness of the pulse the time which the pulse takes in crossing the electron is  $\delta/c$ , and the total energy,  $E'$ , becomes

$$\frac{2}{3} \frac{e^4}{m^2} \frac{X^2 \delta}{c^2}$$

But the energy in the primary pulse per unit area is given by

$$E = \frac{1}{4\pi} \frac{X^2 \delta}{c^2}$$

$$\text{Hence} \quad E' = \frac{8\pi}{3} \frac{e^4}{m^2} E \quad (80)$$

This is the energy radiated by a single electron. If there are  $N$  electrons per unit mass and we assume that they do not influence each other's motion the total scattered radiation per unit mass of radiator will be

$$\frac{8\pi}{3} \frac{Ne^4}{m^2} E \quad . \quad (81)$$

This equation obviously enables us to calculate the number of electrons contained in unit mass of the radiator, if the ratio  $E'/E$  of the scattered to the primary radiation can be measured.

Since it is found by experiment that the qualities of the scattered and the primary radiations are the same, the amount of ionization which they produce in a given volume of gas will be simply proportional to the energy of the rays. Thus we can compare their intensities by allowing them to enter in turn a suitable ionization chamber and observing the saturation currents produced. These currents will be proportional to the number of ions formed per second by the rays, that is, to the energy of the rays and thus

$$\frac{E'}{E} = \frac{i'}{i}$$

where  $i'$  and  $i$  are the two currents

For a carbon radiator of unit mass  $E'/E = 0.20$  approximately. Assuming  $e = 1.59 \times 10^{-20}$  e.m.u. and  $e/m = 1.77 \times 10^7$ , we have from (81) the number of electrons in one gram of carbon  $= 3.1 \times 10^{23}$

Now the mass of a hydrogen atom is  $1.66 \times 10^{-24}$  gm. and that of a carbon atom, therefore,  $12 \times 1.66 \times 10^{-24}$  gm. or  $2 \times 10^{-23}$

The number of carbon atoms in one gram of carbon is therefore  $\frac{1}{2 \times 10^{-23}}$  or  $5 \times 10^{22}$ . The number of electrons contained in an atom of carbon is therefore  $3.1 \times 10^{23} - 5 \times 10^{22}$  or about 6. It is thus approximately equal to the atomic number<sup>1</sup> of the radiator.

Experiments seem to indicate that, at any rate for substances of small atomic weight, the energy scattered per unit mass is approximately independent of the nature of the radiator. The number of electrons per atom is therefore equal to its atomic number.

\* The atomic number of an element is its number in the series of the elements arranged in order of ascending atomic weights. Thus hydrogen is 1, helium 2, lithium 3, and so on. Except in the case of hydrogen the atomic number is not far removed from one-half the atomic weight. It is found that various relationships between the atomic properties become more exact when the atomic number is substituted for the atomic weight. In fact Aston's experiments on isotopes have shown that the chemical atomic weight is not a fundamental quantity, but only a mean value. Experiment shows that isotopes of the same element have an identical atomic number. The importance of the atomic number was first brought out clearly by the experiments of Moseley (§ 94). On the Rutherford theory of the atom (§ 149) the atomic number is equal to the resultant charge upon the positive nucleus of the atom. Since the atom is neutral as a whole, the number of electrons must equal the charge on the nucleus, that is, it must be equal to the atomic number, as found above.

**88 Interference phenomena with X-rays** The identification of X-rays with light of short wave length naturally led to many attempts to detect variations in the intensity of the X-rays passing through narrow apertures, comparable with the effects obtained under similar circumstances with a beam of light Haga and Windt<sup>(3)</sup> in 1901 made experiments with a V-shaped slit, a few thousandths of a mm wide at its narrowest end, and obtained certain variations of intensity in the resultant photograph which if really due to diffraction would indicate a wave length of the order of  $1.3 \times 10^{-8}$  cm. The experiments are difficult and have never been accepted as decisive, although it is only just to say that the value obtained by these experiments has been confirmed by the method of crystal reflection which we are about to describe. Similarly numerous attempts to obtain regular refraction or reflection with X-rays all led to negative results.

The obstacle in the way of regular refraction or reflection is evidently, if we are to accept Haga and Windt's estimate, the extreme shortness of the wave length of the rays. The ordinary reflection of light by a polished surface depends upon the possibility of rendering the irregularities of the surface negligible in comparison with the wave length of the light. It is obvious that for rays of wave length comparable with the diameters of the individual molecules this is no longer a possibility, and even the best optical surface must present to the Röntgen beam an appearance very like a layer of shot.

It is equally obvious that it would be hopeless to attempt to rule a grating which would produce appreciable diffraction in waves of this wave length. A beam of sodium light of wave length  $5.89 \times 10^{-5}$  cm. is deflected through an angle of some  $19^\circ$  by a grating with 5500 lines to the cm., that is, a spacing of 0.00018 cm. To produce a similar deviation in X-rays would require each of these spacings to be divided into ten thousand spaces, a process mechanically and physically inconceivable. It was not until 1912 that Prof. Laue<sup>(1)</sup> conceived the idea that the regular grouping of the atoms in a crystal, as affirmed by modern crystallography, might provide a natural grating of suitable spacing for the experiment. The problem is of course

much more complicated than that of the ordinary grating in which the spacings are all parallel and all in one plane. The regularity of the crystal grating is in three dimensions instead of only one and may be roughly compared to a pile of gratings one on the top of the other. The mathematical solution is far from simple if attacked directly as by Laue. However a solution was obtained. He shewed that if a narrow pencil of X-rays was made to pass symmetrically through a crystal diffracted rays would emerge in various directions from the crystal and would form a symmetrical pattern of spots arranged according to definite laws on a photographic plate placed perpendicular to the beam.

Laue not being an experimentalist, the theory was put to the test by Friedrich and Knipping in 1913, and emerged

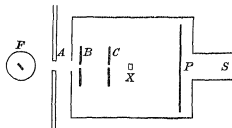


Fig. 64

triumphantly. Their apparatus is indicated in Fig. 64. *F* is the anti-cathode of a powerful focus tube, and the rays are limited to a narrow pencil by passing through a series of slits in the lead screens *A*, *B*, *C*. They then fall on a crystal at *X*. A sighting screen *S* enables the adjustment to be made. A photographic plate is then inserted at *P* and an exposure made lasting for some hours. On developing the plate it was found that the very black central patch made by the undeflected beam of rays was surrounded by a symmetrical pattern of spots as indicated by the theory, some of the spots being deviated by nearly  $40^\circ$  from the direct line of the primary beam.

89. **Theory of Laue's experiment.** Modern crystallographers, following Bravais, have been led to regard the atoms in crystals as arranged with a definite spacial symmetry. All

the atoms of the same sort are regarded as forming a regular system of points in space, the different systems belonging to the different atoms of course interpenetrating. This net-like arrangement is known as a space lattice.

In order that a set of points shall form one of these space lattices they must satisfy certain geometrical conditions. These conditions can be worked out irrespective of any definite knowledge of crystalline structure merely from the general laws to which all regular patterns in space must conform.

It has been shewn that the only method of dividing up space which will satisfy the conditions is as follows. A series of three sets of parallel planes is taken intersecting each other. All the planes in each set are parallel and equally spaced, but the spacings of the different sets need not be the same, and the

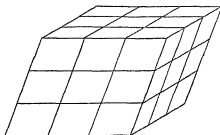


Fig. 65

planes may intersect at any angle. The space is thus divided up into a series of parallelepipeds (Fig. 65) the corners of which form a space lattice.

Let us for simplicity consider the special case, corresponding to the cubic system of crystals, in which the elementary parallelepipeds become cubes, that is, the three sets of planes are equally spaced and intersect at right angles. We have seen that an atom under the action of a Röntgen pulse becomes the centre of a secondary wave of disturbance which spreads out through space. In fact each atom resembles very closely one of Huyghens' "elements".

Consider such an atom at  $O$  (Fig. 66) and take  $O$  as the centre of co-ordinates and the three directions of the space lattice as the axes. If the wave is passing in the direction  $OZ$  it will

strike the three atoms  $O$ ,  $A$ ,  $B$  at the same moment. Let us consider the conditions which must be satisfied for the secondary wavelets from the four atoms  $O$ ,  $A$ ,  $B$ ,  $C$  to co-operate with each other in some direction  $OR$ . For the wavelets from  $O$ ,  $A$ , and  $B$  to co-operate they must arrive at a plane through  $C$  perpendicular to  $OR$  in phase with each other, that is the path differences must each contain a whole number of wave lengths. The actual distances are  $d\gamma$ ,  $d(\gamma - \alpha)$  and  $d(\gamma - \beta)$  where  $\alpha$ ,  $\beta$  and  $\gamma$  are the direction cosines of  $OR$  and  $d$  is the side of the cube. Thus

$$\begin{aligned} d\gamma - d(\gamma - \alpha) &= p\lambda \\ d\gamma - d(\gamma - \beta) &= q\lambda \end{aligned}$$

where  $p$ ,  $q$  are whole numbers, representing the number of complete wave lengths in the given distances. Further, for co-operation with the atom at  $C$ , the path difference between the

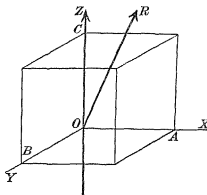


Fig. 66

radiation reaching  $C$  and the scattered wave from  $O$  must also be an integral number of wave lengths, whence  $d - d\gamma = r\lambda$ , where  $r$  is an integer. Thus we have on reduction

$$\frac{\alpha}{p} = \frac{\beta}{q} = \frac{1 - \gamma}{r} = \frac{\lambda}{d} \quad (82)$$

Since  $p$ ,  $q$ ,  $r$  are integers,  $\alpha$ ,  $\beta$  and  $(1 - \gamma)$  must bear to each other a simple ratio.

When this condition is fulfilled the secondary wavelets will reinforce each other in the direction  $OR$  and there will be a spot on the photographic plate where this line meets it. From



the position of the spot it will be possible to deduce the values of the direction cosines (knowing the distance of the plate from the crystal). Hence the theory can be brought to the test. On making the experiment it was found that in no case was it necessary to assign a greater value than 10 to the parameters  $p$ ,  $q$ ,  $r$ , in order to give to the quantities  $\alpha$ ,  $\beta$ , and  $(1 - \gamma)$  an integral ratio.

The problem is really more complex than we have indicated, and the exact interpretation of the diffraction pattern obtained on the plate becomes a matter of some difficulty and uncertainty. Fortunately a slight modification of the experiment can be made which gives not only a much simpler method of regarding the phenomena but also results capable of yielding more definite information.

**90 Reflection of X-rays by crystal planes. Experiments of Bragg.** Shortly after the publication of the work of Laue,

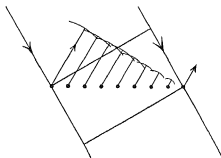


Fig. 67

W. L. Bragg (5) discovered that X-rays could be regularly reflected by the cleavage planes of crystals when the rays were incident on the surface at nearly glancing angles. If we return to Fig. 65 it will be noticed that along certain planes drawn in the crystal, the construction planes, for example, the atoms are thickly studded, that is to say, these planes pass through a considerable number of atoms. It is possible to draw other planes in the crystal, such for example as those drawn through opposite edges of the elementary parallelepipeds, which contain somewhat fewer but still considerable numbers

of atoms. These planes are closely related to the surfaces of the natural crystal. They represent lines along which the crystal will cleave or split with comparative ease, and all are parallel to possible faces on the crystal. It is thus comparatively easy to identify them when the system of symmetry of the crystal is known.

Consider now a parallel beam of X-rays falling on one of these thickly studded planes represented in section by the dots in Fig. 67. As the wave front passes over each atom in turn, it becomes as we have seen the source of a secondary pulse similar in character to that of the primary radiation. The separate secondary pulses will combine to form a wave front which at any appreciable distance from the plane will be practically plane, and will be inclined to the reflecting plane at an angle equal to that of the incident wave. We have in fact a reproduction of Huyghens' construction for the reflected wave from a plane surface, with the exception that in the case of light we regard the reflecting elements as perfectly continuous while in the case of X-rays owing to the much shorter wave length it is necessary to regard them as a finite number of definite points. The energy in the reflected wave, as we may call it, will obviously be proportional to the number of atoms per unit area in the plane.

There are many ways in which we can draw planes in the crystal but only in those few cases where the planes have some obvious relation to the symmetry of the crystal will these planes contain an appreciable number of atoms, and thus produce any appreciable reflection. Thus we may expect that when a beam of X-rays falls on a crystal the scattered radiation will be emitted in a comparatively few directions corresponding to the thickly studded planes in the crystal. For purposes of calculation we may regard these rays as having been reflected in the different sets of planes. It must be pointed out, however, that this reflection is a volume reflection taking place at all the planes in the crystal. It does not depend for its existence on any such plane on the surface of the crystal, nor indeed on the presence of any polished surface at all.

So far we have only considered the effect of a single plane

The energy scattered by a single plane, however, will be infinitesimally small, and it will only be in the case where the reflected rays from different parallel planes reinforce each other that the effect may be expected to be appreciable. It is owing to the fact that our crystal is in three dimensions and contains a series of planes one above the other all exactly similar, and parallel to each other, that any appreciable effect is produced.

Let  $pp, qq, rr, \dots$  (Fig. 68) be a series of such planes, and let  $PP''$  be a wave front advancing on the crystal in the direction  $PQ$ , making an angle  $\theta$  with the surface  $pp$ . It is obvious that the reflected radiation will be most intense if all the waves from the successive layers reach  $R$  in the same phase, that is, if the difference in path of the rays  $P'Q'Q$  and  $PQ$  is a whole number

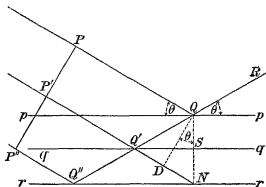


Fig. 68

of wave lengths. Draw  $Q'SN$  perpendicular to  $pp$  and  $Q'D$  perpendicular to  $P'N$ . Then since  $PQ$  and  $QR$  make equal angles with the line  $pp$ , and  $QN$  is perpendicular to  $pp$ ,  $Q'Q$  is equal to  $Q'N$  and the path difference between the two rays under consideration is  $P'Q' + QQ' - PQ = P'Q' + Q'N - P'D$

$$\begin{aligned} &= DN \\ &= QN \sin \theta \\ &= 2d \sin \theta \end{aligned} \quad (83)$$

where  $d$  is the perpendicular distance between the planes. Hence the condition for maximum reflection at any crystal face is that  $2d \sin \theta$  shall be an integral number of wave lengths of the radiation used.

It will be noticed that the problem is exactly analogous to that of the diffraction grating, the various parallel planes acting as lines in the grating. Applying the usual optical principles it can be shown that a very small discrepancy from exact agreement in phase between the separate elements will result in the almost complete extinction of the radiation by interference. The reflected image will therefore be very sharp just as in the case of the grating. Also, exactly as in the case of a grating, each particular wave length will be reflected at some single definite angle.

If the primary X-radiation is homogeneous there will obviously be a series of directions along which the radiation will be reflected, these being obtained by making  $n$  successively equal to 1, 2, 3, . . . in the general equation

$$2d \sin \theta = n\lambda, \quad \dots \quad (81)$$

where  $\lambda$  is the wave length. These will correspond to the spectra of different orders produced by a grating, and may be alluded to as the first, second, etc., order reflection spectra. These spectral lines can be identified as belonging to the same primary wave length by the fact that  $\sin \theta_1 = \sin \theta_2 = \sin \theta_3 = \dots$

The method obviously gives us a means of comparing the wave lengths constituting our primary beam. For if we allow two beams of wave length  $\lambda$  and  $\lambda'$  to fall on the same face of the same crystal they will suffer reflection at angles  $\theta$  and  $\theta'$  respectively, such that  $2d \sin \theta = n\lambda$ ,  $2d \sin \theta' = n\lambda'$ . Hence for the same crystal and the same order of reflection we have

$$\frac{\lambda}{\lambda'} = \frac{\sin \theta}{\sin \theta'} \quad \dots \quad (85)$$

Thus if our primary beam is made up of a number of definite wave lengths, there will be a series of definite angles at which we shall obtain sharp reflection of the rays, each angle corresponding to some definite wave length. If on the other hand the X-rays form a continuous series of wave lengths, there will be a certain range of angles between which reflection will take place. This corresponds to the case of the continuous spectrum

formed by a grating with white light, and the radiation may conveniently be referred to as "white" X-radiation.

It is obvious that the phenomenon is confined to certain definite small limits. Since the maximum value of  $\sin \theta$  is unity, then  $n\lambda/2d$  must be less than 1. Thus reflection will only take place when  $n$  is sufficiently small and  $d$  sufficiently large. In very favourable cases, using the principal planes of the crystal  $d$  may be as much as five times  $\lambda$ , in which case as many as ten spectra may be observed. The intensity however as in the case of an ordinary grating decreases rapidly with the order of the spectrum. It is found experimentally that the distance apart of the planes decreases rapidly as the planes become less fundamental, and eventually becomes so small that there are no values satisfying equation (81) for the wave lengths generally present in a Rontgen beam.

It is evident that if we keep  $\lambda$  constant and use different planes as reflecting planes we can find the relative values of  $d$  for the various crystal systems and thus obtain much light on crystal structure.

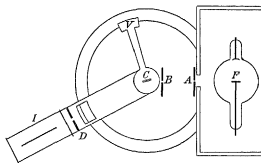


Fig 69

**91. The X-ray spectrometer** The different angles at which reflection can occur may be investigated either by a photographic or by an ionization method, and each has been used by different investigators. The apparatus needed for the ionization method has been perfected by W. H. Bragg and is indicated in Fig. 69. The rays from the anti-cathode of the X-ray tube are limited to a narrow pencil by two lead slits

*A* and *B* These are adjustable by a screw and their width can be read on a suitable scale attached to the screw. The arrangement may be compared to the collimator of a telescope. The crystal is mounted on the table of the spectrometer, as we may call it, at *C*, and its orientation may be read by the vernier *V* on the circular scale of the instrument. The ionization chamber *I* is carried by an arm also pivoted at the centre of the instrument, and the reflected beam can be limited by a third lead slit *D*. The current through the ionization chamber can be measured by an electroscope or electrometer in the usual way. As the intensity of the reflected ray is usually small the ionization chamber is generally filled with some heavy gas such as methyl iodide, in which the ionization produced by

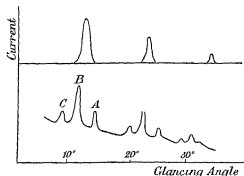


Fig. 70

a given beam of X-rays is more intense than it is in an. If a photographic method is preferred a photographic plate is substituted for the ionization chamber.

In using the apparatus the crystal and the chamber are moved together, the latter of course being always moved through twice the angle of the former. As the glancing angle between the crystal face and the incident beam is gradually increased a point is reached where the electroscope shews a deflection, and the ionization current can be plotted against the glancing angle. If the rays are homogeneous the X-rays will only enter the chamber and the current will only flow at certain definite angles corresponding to the different order of spectra for that particular wave length, and the curve will be discontinuous.

This case is represented by the top curve of Fig. 70, which shews the current through the chamber against the glancing angle  $\theta$ . It will be seen that the curve shews three peaks or "lines" and these three peaks can be identified as being due to the same waves by the fact that  $\sin \theta_1 : \sin \theta_2 : \sin \theta_3$  as 1 : 2 : 3. In general, however, if the radiation is that from an ordinary X-ray tube, it will be made up of certain rays of definite wave lengths together with more or less "white" radiation or radiation of continuous wave length. The curve will then be a continuous curve rising to various peaks or maxima, the height of which affords a rough measure of the intensity of the corresponding wave length in the primary beam. This is shewn in Fig. 70 the bottom curve of which gives the radiation from a platinum anti-cathode. It will be seen that in this very important practical case the rays consist of a mixture of three special wave lengths which are characteristic of platinum, on a background of "white" radiation. If the turning is continued these three peaks appear again in the second order reflections, and again in the third order. It will be noticed that the intensity decreases with the order of the spectrum. These three peaks are characteristic of the platinum anti-cathode. They reappear whatever the nature of the crystal used for the reflection, rock salt, iron pyrites, fluorspar, etc., all yielding the same result. The curves are in fact exactly similar in the three cases, only the scale of the curve depending, as might be expected from the theory, on the nature of the crystal used.

**92 Determination of the wave length of X-rays** The theory so far developed only enables us to compare wave lengths. To determine them in absolute units we must know the distance apart of the planes in our crystal grating. The discussion involves some acquaintance with elements of crystallography, but the argument is briefly as follows.

Taking the case of a simple cube (Fig. 71), the most important faces are (1) the face of the cube itself, (2) the face parallel to a plane through opposite edges of the cube, (3) the face parallel to a plane including one corner of the cube and passing through the diagonal of the opposite face. The develop-

ment of this face gives rise to regular octahedra and is exceedingly common on cubic crystals. The three sets of planes are denoted in crystallography as  $\{100\}$ ,  $\{110\}$ , and  $\{111\}$ , respectively.

Now crystallographers recognize three classes of cubic symmetry,

(1) the simple cube arising from a simple cube lattice such as we have already described,

(2) a cube with a single particle at the centre, known as the cube centred lattice,

(3) a simple cube with a particle at the centre of each face this is known as the face centred lattice.

Now the ratios of the distances between two successive planes for the three sets of planes corresponding to the systems  $\{100\}$ ,

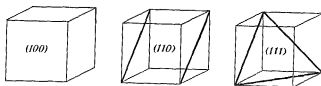


Fig. 71

$\{110\}$ ,  $\{111\}$  will not be the same for the three kinds of lattices. It can be shewn by simple geometry that

$$\begin{aligned} \frac{1}{d_{100}} \quad \frac{1}{d_{110}} \quad \frac{1}{d_{111}} \\ &= 1 \cdot \sqrt{2} \quad \sqrt{3} \text{ for simple cube lattice} \\ &= 1 \quad \frac{1}{\sqrt{2}} \quad \sqrt{3} \text{ for a cube centred lattice} \\ &= 1 \quad \sqrt{2} \quad \frac{\sqrt{3}}{2} \text{ for a face centred lattice} \end{aligned} \quad (86)$$

Now by using the same homogeneous X-radiation for the three faces  $\{100\}$ ,  $\{110\}$ ,  $\{111\}$  respectively we can by (83) find the ratios of  $d_{100}$ ,  $d_{110}$ ,  $d_{111}$ . We can thus identify for any given crystal, by applying the above results, the particular order of cubic symmetry to which the crystal belongs.

Let us apply these results to the important sylvine group, comprising rock salt (NaCl), sylvine (KCl) and the corre-



sponding bromides and iodides. These are chemically and crystallographically similar and may reasonably be expected to have the same structure. In the case of sylvine the measurements would indicate that it has the simple cubic structure. With rock salt, however, we meet a new phenomenon. The reflections from the  $\{111\}$  faces give a weak first order spectrum, a strong second, a weak third, a strong fourth, and so on. Judging only by the strong spectra we should assign to rock salt the simple cube lattice. Judging by the weak first order spectrum it would be a face centred lattice. How are the two results to be reconciled with each other and with the result for the crystallographically identical sylvine?

W. L. Bragg made the suggestion that the points making up the crystal structure were not molecules but atoms of the constituents of the salt. Now we know that the intensity of the scattered radiation from an atom is proportional to the number of electrons in it and therefore to the atomic number. Thus the reflections from the sodium planes ( $\text{Na} = 11$ ) will be comparatively weak and those from the chlorine planes ( $\text{Cl} = 17$ ) will be comparatively strong. There will, however, be no such difference in the case of sylvine, since the atomic number of potassium (19) is very near that of chlorine. In fact, since the compound  $\text{KCl}$  is formed by the passage of an electron from the potassium atom to the chlorine atom (see § 155), the number of electrons in each will be the same, and their radiating powers will be identical. He found that all the results could be accounted

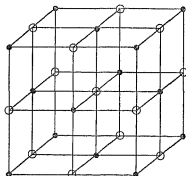


Fig. 72

for by assigning to both crystals the structure indicated in Fig. 72, the metallic atoms being represented by dots, the chlorine atoms by circles. If the dots and the circles produce identical effects as is practically the case with sylvine, the system becomes a simple cube lattice. When the particles are different, however,

the case corresponds to that of an optical grating in which every odd ruling is made somewhat wider than the even ones. In this case, as we know, a second set of spectra corresponding to a grating with twice the actual grating space appears, superimposed upon the normal spectra, the deflection of the first order spectrum being approximately half that of the normal first order spectrum.

Accepting this structure for the rock salt crystal we see (considering the adjacent cubes in all directions) that each sodium atom is associated with eight of the small cubes into which the figure can be divided, and assuming its mass to be equally divided among the cubes, one-eighth of the mass is included in each cube. There are four sodium atoms associated with each small cube and thus each small cube includes the mass of half an atom of sodium, and therefore half a molecule of the compound sodium chloride. Thus the whole structure of Fig. 72 represents four molecules.

The distance apart of the planes bounding the small cubes is obviously  $d_{100}$ , all the planes being exactly similar. Hence the volume of each small cube is  $(d_{100})^3$ . The mass associated with each small cube is one half that of the sodium chloride molecule, that is  $\frac{1}{2}(23 + 35.5) \times$  (the mass of the hydrogen atom). The mass of the latter as we have already seen (§ 25) is  $1.66 \times 10^{-24}$  gm.

Hence if  $\rho$  is the density of the rock salt crystal ( $= 2.17$ ) the mass of the cube  $= \rho (d_{100})^3 = 29.3 \times (1.66 \times 10^{-24})$

and

$$d_{100} = 2.814 \times 10^{-8} \text{ cm.}$$

For the most pronounced radiation from platinum the glancing angle for the first order spectrum using the  $d_{100}$  planes of rock salt is  $11.4^\circ$ . Hence substituting in the equation  $\lambda = 2d \sin \theta$  the wave length of this particular X-radiation is given by

$$\lambda = 1.10 \times 10^{-8} \text{ cm.}$$

**93. The X-ray spectra.** The continuous background. We have seen that the X-ray spectrum emitted when cathode rays impinge on a target consists, to use optical phraseology, of a series of bright lines superimposed on a continuous luminous background. The lines are characteristic of the substance forming

the target and constitute its X-ray spectrum. The background is independent of the nature of the target except for the fact that its intensity is proportional to the atomic number of the element of which the target is made. For a given target the intensity of the radiation is proportional to the square of the P D across the tube, and to the current passing through it. The energy in the radiation is, however, only a minute fraction (less than  $\frac{1}{10000}$ ) of that of the incident cathode rays, the remaining portion of the energy appearing in the target in the form of heat.

The distribution of intensity in the spectrum is indicated in Fig. 73(b). The form of the curves is reminiscent of the dis-

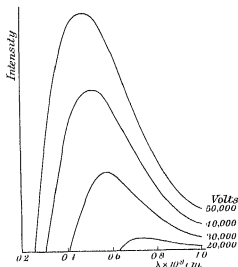


Fig. 73

tribution of energy in the spectrum of black body radiation, but there is still considerable doubt as to the equation to the curves. The maximum of the curve moves in the direction of shorter and shorter wave lengths as the P D across the tube is increased.

It will be noticed that the curve falls to zero at some definite wave length, which depends on the P D used to excite the tube. There is thus for each P D a minimum value for the wave length.

of the radiation emitted, or in other words a maximum frequency, which cannot be exceeded. Very careful investigation of this end part of the spectrum by Hull(7) and others has shown that this frequency  $\nu$  is directly proportional to the applied  $P.D.$  If  $V$  is the potential difference in volts it was found that over the whole range of potentials employed (from 24,000 to 100,000 volts) the relation could be expressed by the formula

$$V = 4.131 \times 10^{-15} \nu,$$

or converting volts to absolute e.s.u. and multiplying both sides by  $e$ , we have

$$\begin{aligned} Ve &= (1.377 \times 10^{-17}) \times (4.774 \times 10^{-10}) \nu \\ &= 6.55 \times 10^{-27} \nu \end{aligned}$$

Thus the maximum frequency of the radiation emitted is related to the maximum energy of a cathode particle in the tube by the quantum relation, energy =  $Ve = h\nu$ , and the value of Planck's constant  $h$  obtained in this way agrees accurately with that determined from photo-electric phenomena. It will be noted that in both cases the law is a direct expression of an experimental relationship, and is independent of any theory of the effect.

Although numerous attempts have been made no generally accepted theory of the continuous radiation has yet been evolved along the lines of the quantum theory. The classical theory has already been considered in detail. With the exception of the existence of a maximum frequency (which is not indicated by classical conceptions) the classical theory seems to provide an adequate representation of the phenomena of the continuous radiation, and of scattered radiation.

**94 The X-ray spectra.** The characteristic radiations. It had been known for some time before the discovery of the X-ray spectrometer made it possible to determine the wave length of X-radiations, that the X-radiation given out when cathode rays impinge on a target or anti-cathode of any given substance contains groups of rays which are characteristic of the substance of the target. These characteristic rays had been

detected and classified by their various absorbabilities in some standard substance, usually aluminium, and were found to fall into two classes. The more penetrating characteristic radiation of the element was known as its *K* radiation, while the less penetrating type was called the *L* radiation of the element. Each type of radiation was found to be, to within the limits of accuracy of the absorption experiments, homogeneous.

The methods of X-ray spectroscopy obviously enabled the investigation of these homogeneous or characteristic radiations to be pursued with greater accuracy and certainty than could be achieved by mere absorption measurements, and made possible the actual determination of the wave lengths of the radiations. To avoid the necessity of making and evacuating a large number of tubes the various anti-cathodes can be mounted on a sort of trolley which can be controlled from outside the tube by a magnet. By moving the trolley to different positions each anti-cathode in turn can be brought to the focus of the cathode beam, and its emission investigated.

The ionization method employed by Bragg is obviously less suited to investigate what may be called the line structure of the radiation than the photographic method, and the latter is almost exclusively employed in these researches. Assuming the wave length of the radiation to have been previously roughly determined the crystal is adjusted so that the incident beam of X-rays from the anti-cathode falls upon it at approximately the correct glancing angle. The crystal is then rotated continuously backwards and forwards through a few degrees about this mean angle during the whole of the exposure. It is evident that whenever during its rotation it makes with the incident beam an angle which is the correct glancing angle for any of the wave lengths radiating from the anti-cathode selective reflection will take place, and a line will be formed on a photographic plate placed in a suitable position to receive the reflected radiation. Thus if the incident radiation consists of a mixture of rays of various wave lengths each will record itself as a single line on the photographic plate, and an X-ray spectrum (Fig. 45) will be formed, closely resembling the bright line spectrum produced when the light from a vacuum tube is photographed.

through an ordinary spectroscope. It is obvious that if the dimensions of the apparatus are known the corresponding glancing angle for each line can be determined, and the wave length deduced.

When examined by the spectrometer it is found that neither the  $K$  nor the  $L$  radiations are homogeneous. The  $K$  radiation consists of four principal lines, the  $L$  radiation shows fifteen or more. Thus the  $K$  spectrum of tungsten, the element most often employed in the target of an X-ray tube, shews four  $K$  lines

$$K_{\alpha_1} = 0.2134, \quad K_{\alpha_2} = 0.2086, \quad K_{\beta_1} = 0.1634, \quad K_{\beta_2} = 0.1574,$$

all in Ångström units, and an  $L$  spectrum (Fig. 45) of thirteen distinct lines ranging from 1.6750 to 1.0265 Å. The progress made in X-ray spectroscopy is so great that relative values can be relied upon to one part in 10,000. The absolute values depend on Bragg's determination of the grating space in sodium chloride (§ 92) and are thus of a lower order of accuracy.

The outstanding feature of the X-ray spectra is their great similarity to each other. In fact, with some minor exceptions, the characteristic spectrum of one element differs from that of another only in being displaced bodily in the spectral scale, the wave length of the various lines becoming smaller as the atomic number of the element becomes greater. Moseley (8), to whom the first extensive series of observations is due, found that if  $\nu$  is the frequency of some particular line in the spectrum, say the  $K_{\alpha_1}$  line for example, then its value for any element can be expressed by the equation

$$\nu = a(N - b)^2, \quad (87)$$

where  $N$  is the atomic number of the element, and  $a$  and  $b$  are constants for that particular line. The value of  $a$  varies as we pass from one line to another, say from the  $K_{\alpha_1}$  to the  $K_{\alpha_2}$  line. The value of  $b$  is the same for all lines of the same series. For the  $K$  series it has a value very nearly equal to unity, for the  $L$  series its value is about 7.4. These relations are not quite exact, but if  $\sqrt{\nu}$  is plotted against  $N$  a perfectly smooth line is always obtained, which, however, shews a slight curvature for large values of  $N$ .

The  $K$  radiation has been measured for all elements of higher

atomic number than sodium<sup>(9)</sup> and the  $L$  radiation for elements of higher atomic number than zinc<sup>(10)</sup>. The difficulty in the way of extending the series still further is the great absorbability of the characteristic radiations from elements of low atomic number. In addition a third series of radiations, the  $M$  radiation of still greater wave length than the  $L$  series, has been measured for elements of high atomic number. For tungsten the  $M$  radiations vary from 6.976 to 6.091  $\text{\AA}$  U<sup>(11)</sup>. There is some evidence of the existence of a high frequency, or  $J$  radiation<sup>(12)</sup>.

These characteristic radiations are, of course, all superposed upon the continuous spectrum emitted by the radiator and described in the previous section. When investigated by the

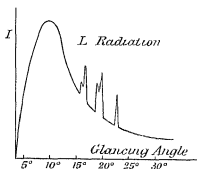


Fig. 74

photographic method, the spectrum appears as a number of dark lines crossing a grey background. By the ionization spectrometer method, the intensity curve shows a series of sharp peaks superimposed upon curves of the type of Fig. 73. This is indicated in Fig. 74, which shows the radiation from a tungsten target excited with a voltage rather smaller than that required to generate the  $K$  lines of tungsten. The various  $L$  peaks are well shown.

**95. The absorption of X-rays.** If a sheet of any substance is interposed in the path of a homogeneous beam of X-rays the intensity of the beam is diminished, and falls off exponentially with the thickness of the sheet. Thus if  $I_0$  is the initial intensity

of the beam,  $I$  its intensity after passing through a thickness  $d$  of material

$$I = I_0 e^{-\mu d}, \quad (88)$$

where  $\mu$  is the coefficient of absorption of the radiation in the particular absorbing substance. The value of  $\mu$  for radiation of any wave length can be measured conveniently with Bragg's spectrometer. The instrument is adjusted so that radiation of the desired wave length falls on the slit of the ionization chamber, and the absorbing substance, in the form of thin sheets, is placed in the path of the reflected ray, between the crystal and the ionization chamber.

It is found experimentally that the absorption depends only on the number of atoms of the substance in the thickness of the absorbing layer, and is independent of their state of aggregation. Thus  $\mu/\rho$ , where  $\rho$  is the density, is constant for a given substance and independent of any changes in density due to its physical condition.  $\mu/\rho$  is called the mass coefficient of absorption. The absorption can obviously be expressed in the form  $I = I_0 e^{-\frac{\mu}{\rho} m}$ , where  $m$  is the mass of unit area of the absorbing sheet.

It is necessary to distinguish carefully between the portion of the energy of the incident beam which is actually absorbed or transformed in the absorbing substance, and that portion which is merely scattered in radiation of the same quality as that of the incident beam. As the scattered radiation is dispersed in all directions, only a fraction of it, depending on the angle subtended at the absorbing sheet by the aperture of the ionization chamber, will enter the latter, and the beam will thus suffer a diminution in intensity from this cause alone. If the experiment is arranged so that only an inappreciable fraction of the scattered radiation enters the measuring chamber the coefficient  $\mu$  as thus measured is the sum of two distinct coefficients, the one  $\tau$  measuring the actual absorption, the other  $\sigma$  the scattering. Thus

$$\mu = \sigma + \tau$$

For light elements we have already seen that  $\sigma/\rho$  has a value of about 0.2, and is independent of the wave length of the incident radiation.

If we take some definite absorbing substance and a beam of



homogeneous radiation of large wave length, so large, in fact that it does not excite the characteristic  $L$  radiation of the absorbing substance, it is found that the coefficient of absorption  $\tau$  diminishes rapidly with diminishing wave length, the relation being expressible in the form

$$\frac{\tau}{\rho} = C\lambda^3$$

This is shown by the portion  $M$  of the curve in Fig 75. At a certain perfectly definite wave length, however, there is a sharp and very marked discontinuity in the curve relating  $\tau$  and  $\lambda$  and the absorption rises abruptly to a high value. At this identical wave length the characteristic  $L$  radiation of the absorbing substance is excited for the first time. The energy of this characteristic radiation must be abstracted from the primary beam, and hence the sudden increase in the coefficient of absorption. The particular frequency for which this phenomenon occurs is known as the critical absorption frequency for the given substance. These absorption limits are so sharp that the wave length at which they occur can be measured to an accuracy of at least one part in a thousand. (See Fig 45 and note on p. 116.)

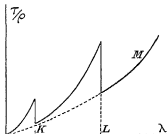


Fig 75

After passing the  $L$  discontinuity the absorption again decreases with the wave length, and again according to a third power law, but with a different coefficient of proportionality, until the wave length is reached at which the  $K$  radiation of the absorber is excited. This gives rise to a  $K$  discontinuity, and the phenomena described above repeat themselves. For elements of very high atomic number an  $M$  discontinuity is observed corresponding to the excitation of the characteristic  $M$  radiation. The absorption curve for varying wave lengths thus has the appearance shown in Fig 75 and the relation may be expressed by the formula

$$\frac{\tau}{\rho} = (C_K + C_L + C_M) \lambda^3, \quad (89)$$

where  $C_K$ ,  $C_L$ , and  $C_M$  are constants for the given substance, which come into action when the wave length of the incident radiation is less than the corresponding  $K$ ,  $L$ ,  $M$ , absorption limits

It may be mentioned, in passing, that the absorption limit has a wave length slightly shorter than that of any of the lines in the corresponding series. No line of the  $K$  series is excited until the  $K$  limit is reached, but on reaching it all the lines are produced simultaneously. Close investigation has shown that the  $L$  limit is, in fact, a triple one consisting of three peaks very close together (Fig. 76), while the  $M$  discontinuity consists of

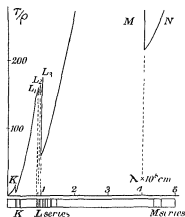


Fig. 76

no less than five such peaks. The relation between the frequencies of the same absorption limit for absorbing elements of different atomic number is given by Moseley's relation

$$\nu = a(N - b)^2$$

For radiation of constant wave length the absorption varies as the cube of the atomic number of the absorbing substance. The full relation for the absorption of radiation of wave length  $\lambda$  by an element of atomic number  $N$  is thus given by

$$\frac{\tau}{\rho} = (C_K + C_L + C_M) N^3 \lambda^3. \quad (90)$$

**96. Characteristic secondary radiation.** As we have seen in the last section the characteristic radiation of an element

may be excited not only by the impact of cathode rays in a discharge tube but also by the action of a beam of X-rays, providing that the latter is of suitable wave lengths. The rays so excited may be described as characteristic secondary rays, to distinguish them from the purely scattered secondary radiation already described (§ 85).

Much work had already been done on these characteristic secondary rays by Barkla (13) and others, before the phenomena of crystal reflection gave us a means of actually measuring their wave lengths. In order to identify the different radiations their absorbability in a light substance such as aluminium, which has no discontinuities within the range of wave lengths usually employed, was used as a test both of their homogeneity and of their wave length.

If the absorption of a beam of X-rays is measured using different thicknesses of the absorbing substance we can get a rough test of the homogeneity of the beam. If we have a primary beam of rays containing both hard and soft rays the latter will be absorbed by the first few thicknesses of material while the former being more penetrating will be largely transmitted. The beam will thus become relatively richer in the more penetrating components as it passes through greater thicknesses of material, and hence its absorption will not follow an exponential law. It was found by Barkla that the absorption of the primary rays from an ordinary focus tube was not exponential, and the rays were thus presumably complex. It was found, however, that the secondary radiation given out by a copper radiator for example when illuminated by a beam of primary X-rays was absorbed very accurately according to an exponential law, and was, therefore, homogeneous. For this reason the characteristic secondary radiation from a radiator is often described as its "*homogeneous radiation*". As we have seen, neither series of characteristic radiations is strictly homogeneous. As, however, the lines in the same series do not differ very widely in wave length we should not expect to disentangle them by the comparatively crude absorption method.

In this way the existence of the two series of radiations was recognized, and the characteristic *K* radiations of all the elements

from sulphur to barium, and the  $L$  radiations from silver to bismuth investigated and their absorption coefficients in aluminium determined. Aluminium was used as a standard of absorption because in the first place it can readily be obtained in sheets of any required thickness, and in the second place owing to its small atomic weight its own characteristic radiations are not excited in appreciable quantity and thus do not interfere with the results.

It was found as a result of these investigations that the coefficient of absorption in aluminium of the characteristic radiation of a given element was inversely proportional to some power (the fifth or sixth) of the atomic number. This follows directly from the laws already stated, the coefficient of absorption being proportional to  $\lambda^3$  while the wave length of a given characteristic ray is inversely proportional to the square of the atomic number of the element emitting it.

It was found that in order to excite the characteristic radiation in an element it is necessary that the incident primary beam should have a shorter wave length than that which it is wished to excite. Thus the radiation from copper cannot be excited by the characteristic radiation from nickel, or even by the characteristic radiation from copper itself. It is, however, excited by the characteristic radiation of zinc, which of course has a slightly shorter wave length. The analogy with the phenomenon of optical fluorescence is obvious, and on this account some writers refer to the characteristic secondary radiation as the *fluorescent* radiation.

These phenomena were demonstrated by Barkla with the simple apparatus illustrated in Fig. 77. The primary rays from a focus tube  $F$  fall on a radiator  $R_1$  and thence through an aperture in a lead screen  $L$  on to a second radiator at  $R_2$ . The radiation from  $R_2$  can be measured by a gold leaf electroscope of simple type placed at  $E$  out of the direct line of the rays from  $R_1$ . The purely scattered radiation from  $R_2$  is generally too weak to produce any appreciable ionization in  $E$ , the energy scattered by a radiator being normally only a very small fraction (1 per cent or so) of that which it emits when its fluorescent radiation is excited. If, however, the radiation from  $R_1$  is of suitable

quality to excite the characteristic radiation in  $R_2$  the electroscope will lose its charge at a rate which is proportional to the intensity of the fluorescent radiation from  $R_2$ . Thus if  $R_2$  is copper and  $R_1$  is nickel there will be practically no effect on the electroscope  $E$ , but if the nickel radiator is replaced by one of zinc a large effect is obtained. By placing aluminum screens of various thicknesses in front of  $E$ , the coefficient of absorption of the rays can be measured. The apparatus just described is of historic interest, but it has now been completely superseded by the more accurate spectroscopic method described in § 91.

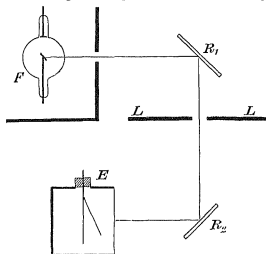


FIG. 77

It has been shown by the author that unlike the scattered radiation the homogeneous radiation is emitted uniformly in all directions round the radiator.

**97. Conditions for the direct excitation of characteristic radiation** As we should expect from the quantum relation the characteristic radiation of a given element when used as an anti-cathode is only excited if the incident cathode rays reach a sufficiently high velocity. For cathode rays of smaller velocity than this only the "general" radiation is given out. The matter was first investigated by Whiddington (14) using apparatus similar to that shown in Fig. 78.

The cathode rays were generated in the bulb *A*, and passed through a narrow hole into the brass cylinder *B* which was wound as a solenoid. By sending suitable currents through the solenoid magnetic fields of calculable intensity could be applied at right angles to the path of the rays, which were deviated by amounts depending on their velocity, and thus spread out into a magnetic spectrum each line of which corresponded to some definite known velocity of the cathode particles. By suitably adjusting the field, particles of any required velocity could be made to fall on the small hole *d* and so on to an anti-cathode at *c*. The X-rays generated passed out through a thin aluminium window *w* into an ionization chamber *I*. If the incident cathode

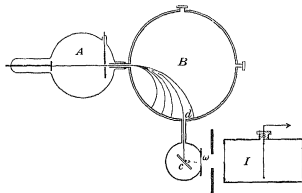


Fig 78

rays were too slow to excite the characteristic radiation of the radiator a certain amount of "white" radiation passed into *I*. This, however, was always largely increased when the characteristic radiation was excited and so a sharp increase in the ionization current occurred when the cathode rays reached the critical velocity.

It was found that for every element there was a definite critical velocity which must be attained by the cathode rays before the characteristic radiation was excited. This critical velocity was found to be proportional to the atomic number of the element.

Whiddington has given his final results in the form

$$v_K = 2(N - 2) 10^8 \text{ cm per sec,}$$

$$v_L = (N - 15) 10^8 \text{ cm per sec,}$$

where  $v_K$  and  $v_L$  are the minimum velocities which will excite the  $K$  and  $L$  radiations of an element of atomic number  $N$ . Since the square root of the frequency of the characteristic radiation also varies as the atomic number, this relation shews that the energy necessary to excite radiation of given frequency is proportional to the frequency, in accordance with Planck's law. Owing to the difficulty of determining the exact point at which the characteristic radiation begins to be excited the values for the critical velocity given by Whiddington's equations are about 30 per cent too high.

More recent work by Webster<sup>(15)</sup>, using a spectrographic method, has shewn conclusively that the characteristic radiation is excited when the energy of the incident cathode particle becomes equal to the quantum of energy for radiation of the wave length at which the corresponding absorption discontinuity (§ 95) occurs. The experiments were carried out with an X-ray tube having a rhodium target and excited by means of a battery of a large number of accumulators. The applied potential was thus constant and could be measured with high accuracy. The maximum energy of a cathode particle in the discharge was thus  $Ve$ , and is known to the accuracy with which the potential difference  $V$  can be measured. The radiation emitted by the rhodium target was analysed by a spectrometer. It was found that for a potential difference of 23.2 kilovolts no lines of the rhodium  $K$  spectrum were excited, but that when the potential difference was raised to 23.3 kilovolts all the lines of the series appeared simultaneously.

Now the wave length  $\lambda$  for which  $Ve$  is the quantum of energy is given by the relation

$$Ve = hc/\lambda$$

Substituting in this equation, the value of  $\lambda$  corresponding to a p.d. of 23.3 kilovolts is found to be  $0.533 \times 10^{-8}$  cm. which is the value found directly for the  $K$  discontinuity of rhodium by absorption experiments. The wave lengths of the  $K$  lines of rhodium range from 0.616 to  $0.534 \times 10^{-8}$  cm. Thus a given line in the spectrum is not excited when the energy in the cathode particle becomes the quantum for the ray concerned, but only when it reaches that of the critical absorption frequency.

**98. The theory of X-ray spectra** The application of the quantum principle to the phenomena described in the preceding sections leads at once to a very convincing explanation of the characteristic X-ray spectra. The work which must be done to extract an electron from the atom will depend on the forces which hold it bound, and hence on its position within the atom. Let us suppose that for the most firmly bound electrons, which we will call the  $K$  electrons for short, this work is equal to  $w_K$ . The smallest frequency which the incident radiation may have if it be able to effect this removal is therefore  $\nu_K = w_K/h$ , where  $h$  is Planck's constant. We may assume that if the quantum of energy is insufficient to produce this ionization the electron will be unaffected by the radiation, and will absorb no energy from it. Thus if the wave length of the incident radiation is greater than that corresponding to a frequency  $\nu_K$ , no energy will be absorbed from it by the  $K$  electrons. As soon, however, as the frequency increases to the critical value, absorption by the  $K$  electrons begins, and there is thus a sudden marked increase in the coefficient of absorption at this critical frequency. Thus the  $K$  absorption discontinuity marks the point at which the  $K$  electrons are capable of abstracting energy from the incident X-radiation. Similar considerations apply to the other absorption discontinuities.

Thus each discontinuity corresponds to some definite position, or level, within the atom where electrons are to be found, the "level" being characterized by the work which must be done to extract an electron from it. This energy is calculable, without ambiguity, from the critical absorption frequencies by the relation

$$w_c = h\nu_c,$$

where  $\nu_c$  is the critical frequency, and this calculation is confirmed by the direct measurements made with cathode particles and described in the previous section (§ 97). The comparatively small number of discontinuities and their great sharpness indicates that the levels which may be occupied by electrons are comparatively few, and their position very sharply defined. The existence of such levels is thus a necessary deduction from the phenomena of X-ray absorption, and does not depend on any theory of atomic structure.



The expulsion of an electron from, say, the  $K$  level will leave a vacancy which will be filled up by some electron, either from outside the atom or more probably, and hence more frequently, by an electron from one of the higher levels. Let us suppose, for example, that the electron falls into the vacant space from the  $L_1$  level. Energy will thus be liberated, in amount equal to the difference between the work necessary to extract an electron from the  $K$  level, and that necessary to extract an electron from the  $L_1$  level, that is to say, to  $w_K - w_{L_1}$ . On the quantum theory this will be radiated in the form of homogeneous radiation the frequency of which will be given by

$$h\nu = w_K - w_{L_1} = h\nu_K - h\nu_{L_1} \quad (91)$$

$\nu$  should thus be the frequency of a line in the  $K$  series of the element. Now, as we have seen, all the quantities in this equation can be determined to an accuracy of at least one part in a thousand. It provides, therefore, a very searching test of the validity of our reasoning.

The experimental data are most complete for tungsten, since this metal is the usual target in an X-ray tube. The values of the  $K$  and  $L_1$  discontinuities are respectively  $0.1785 \times 10^{-8}$  and  $1.2136 \times 10^{-8}$ . We can put equation (91) in the form  $\frac{1}{\lambda} = \frac{1}{\lambda_K} - \frac{1}{\lambda_{L_1}}$ , where  $\lambda$  is the wave length of the radiation which should be emitted. The value of  $\frac{1}{\lambda_K} - \frac{1}{\lambda_{L_1}}$  is  $4.792 \times 10^8$ , and the value of  $\lambda$  should thus be the reciprocal of this, that is  $0.2086 \times 10^{-8}$ . The wave length of the  $K_{\alpha_1}$  line is found, by direct measurement, to be

$$0.2086 \times 10^{-8}$$

Equally satisfactory agreement is obtained for the other lines of the  $K$  spectrum. Fig. 79 indicates the origin of the different  $K$  lines, the levels being indicated diagrammatically by horizontal lines. This theory, which is due to Bohr, has been applied

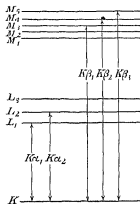


Fig. 79

with equal success to the more complicated  $L$  radiations. In the case of the  $L$  radiation we have three possible final levels corresponding to the three  $L$  discontinuities.

The energy characterizing each level in the atom of a given element can, as we have seen, be determined experimentally either from the critical absorption frequencies, or from the critical energy which a cathode particle must possess to be able to eject an electron from the given level. The results obtained by the two methods are in good agreement. A third method, which promises equal accuracy, is provided by the phenomena of corpuscular secondary radiation described in the following section. The values for the different levels are thus experimental data, and are independent of any particular theory of the structure of the atom. They provide in fact a series of tests which any such theory should be able to satisfy.

The custom has grown up of measuring energy, especially when dealing with such subjects as atomic levels, in "volts." Thus an electron which has fallen through a P.D. of 20,000 volts is said to have an energy of 20,000 volts. Similarly the energy of the  $K$  level of rhodium is said to be 23.3 kilovolts. The nomenclature is then further extended to include radiation, and radiation of wave length  $0.533 \times 10^{-8}$  cm. for which the quantum of energy is 23.3 kilovolts is sometimes described as 23.3 kilovolt radiation. As in many of the experiments the energies are actually measured by the P.D. through which an electron falls, this method has obvious conveniences. The "volts" can be reduced to ergs by converting the volts to e.s.u. and multiplying by the electronic charge in e.s.u.

**99 Secondary corpuscular radiation.** In addition to the scattered and homogeneous secondary radiations which are themselves X-radiations, a beam of X-rays when falling on a substance also gives rise to a very easily absorbable radiation which can be deflected by a magnetic field, and can thus be shown to consist of negatively charged electrons. The velocity of these electrons can be measured by the application of equation (37). These corpuscular rays are all absorbed within a cm. or so of gas, and hence the ionization they produce is very intense.

TABLE VI

Wave lengths and absorption coefficients of characteristic X rays

(The wave lengths are taken from the papers of Siegbahn's. The absolute values depend on Bragg's determination of the grating space of a rock salt crystal (§ 92).)

Element with atomic number	Wave length of characteristic radiations $\cdot 10^8 \text{ cm}$							
	K series			L series				
	$K_{\alpha}$	$K_{\beta}$	Absorp tion limit	$L_{\alpha_1}$	$L_{\alpha_2}$	Absorption limits		
11 Na	11.88	11.59	—	—	—	—	—	—
13 Al	8.42	7.95	7.95	—	—	—	—	—
20 Ca	3.355	3.067	—	—	—	—	—	—
24 Cr	2.290	—	2.067	—	—	—	—	—
26 Fe	1.937	1.711	1.710	—	—	—	—	—
27 Co	1.790	1.606	1.602	—	—	—	—	—
28 Ni	1.659	1.484	1.48	—	—	—	—	—
29 Cu	1.541	1.377	1.375	—	—	12.72	13.1	—
30 Zn	1.436	1.281	—	12.34	—	—	—	—
45 Rh	0.6166	0.5342	0.543	4.588	3.936	—	—	—
46 Pd	0.5885	0.5102	0.507	4.479	3.716	—	—	—
47 Ag	0.5626	0.4959	0.485	4.155	3.515	3.26	3.50	3.69
48 Cd	0.5383	0.4647	0.463	3.959	3.328	—	—	—
50 Sn	0.4938	0.43	0.424	3.604	2.995	2.77	2.99	3.15
74 W	0.2134	0.1790	0.1785	1.485	1.096	—	—	—
78 Pt	0.1898	0.1574	0.157	1.323	0.958	0.89	0.932	1.070
82 Pb	—	—	0.140	1.186	0.842	0.780	0.813	0.949
92 U	—	—	0.105	0.922	0.615	0.568	0.592	0.721

TABLE VII

Wave length $\lambda \cdot 10^8$	Mass absorption coefficient $\tau/\rho$		
	Al	Cu	Ag
0.226	0.283	1.70	5.53
0.245	0.312	2.24	9.29
0.396	0.860	—	29.6
0.465	—	—	47.8
0.491	1.71	20.9	103
0.562	2.50	26.7	144
0.612	3.33	34.6	196
1.101	20.6	186	86
1.313	30.6	273	152.5

The electrons are not emitted equally in all directions. If a very thin radiator is used (such as a sheet of gold leaf) it is found that, just as in the case of the scattered radiation, considerably more of the corpuscular radiation emerges on the emergence side than on the incidence side of the radiator. The electrons are, therefore, projected from the atom with a component velocity in the direction of the primary beam.

Taking the theory of X-rays already propounded, the electric force in the primary pulse will be at right angles to its direction of propagation. The electrons will, therefore, have an acceleration in this direction, which if their attachment to the atom is sufficiently weak will cause them to be projected in this direction, that is at right angles to the primary beam. This lateral projection is extremely well shown in photographs taken by the expansion method of C. T. R. Wilson and shown in Fig. 18. The primary beam, which is invisible, passes across the gas from left to right. The tracks of the electrons ejected by the rays are revealed by the condensation of water upon them. It will be seen that each of these tracks begins nearly normal to the line of the beam.

There is however a magnetic field in the pulse, so that when the particles have been projected they are acted upon by a magnetic field. It is easy to show that the direction of this field will be such as to deflect the particles towards the direction in which the primary X-rays are travelling. In addition to their lateral velocity the particles will thus have a component in the direction of the primary rays.

The matter can easily be dealt with numerically by Planck's theory. The energy absorbed by the electron is  $h\nu$  where  $\nu$  is the frequency. Since this energy was travelling with a velocity  $c$  in the direction of the rays it has a momentum  $h\nu/c$  which is also absorbed by the electron. Hence if  $u$  is the forward velocity of the electron and  $m$  its mass we have

$$mu = \frac{h\nu}{c} \quad (92)$$

But if  $v$  is the velocity of projection due to the absorbed energy  $h\nu$

$$\frac{1}{2}mv^2 = h\nu.$$

$$\therefore \frac{u}{v} = \frac{v}{2c} \quad (93)$$

For the particles projected by X-rays  $v$  is of the order of  $10^{10}$  cm per sec. Thus  $u/c = \frac{1}{6}$ , which is approximately the value obtained by direct experiment.

Since the electrons are projected mainly in a sideways direction, the fact that they emerge from both surfaces of the radiator is due to the deflections they suffer during collision with the molecules of the radiator. Since, however, they have a component of velocity in the forward direction there will always be a preponderance of electrons on the emergence side of the radiator.

The secondary corpuscular radiation bears the same relation to the incident X-radiation that the photo-electrons bear to light. Owing to their much higher speed, however, the distribution of velocities among the corpuscular radiations can be determined more directly and with greater certainty than for

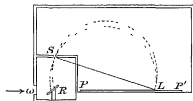


Fig 80

the photo-electrons. The experiments were first carried out by de Broghe(16), and have since been extended by Robinson(17) and others.

The method employed is indicated in Fig 80, which represents the apparatus used by Robinson. The incident beam of X-rays entering the chamber by a window  $\omega$  falls on the radiator at  $R$ . The secondary corpuscular rays emerge from  $R$  in all directions and some pass through a narrow slit  $S$  immediately above the radiator. The photographic plate  $PP'$  is placed film upwards to receive these radiations. The whole box is evacuated to a high vacuum, and is placed in a uniform magnetic field, the lines of which are perpendicular to the plane of the paper. Each of the particles thus describes a circular path. It is easy to show that if the radiator is not too large all particles of the same velocity passing through the slit will be brought to a focus at some point  $L$  on the photographic plate, the plane of which passes through

the radiator. This point will be nearer or further from  $R$  according as the particles have a small or a large velocity. The velocity can easily be calculated from the position of  $L$  when the dimensions of the apparatus and the strength of the magnetic field are known.

Unless the incident X-radiation is homogeneous the phenomena are very complex. When however the radiator is illuminated with homogeneous X-radiation the phenomena are comparatively simple and very interesting. On developing the plate it is found to be crossed by a number of fairly sharp lines, thus shewing that the corpuscular radiation contains groups of electrons of identical velocity. The theory of X-ray spectra already described provides a convincing explanation of these groups of electrons, and their existence provides additional support for the theory.

An electron will be ejected from the  $K$  level of an atom when the incident radiation has a quantum of energy equal to  $w_K$ , the characteristic energy of the level. Suppose the frequency of the incident radiation to be  $\nu$ , where  $\nu$  is greater than  $\nu_K$ , the critical frequency. The  $K$  electron will absorb a whole quantum  $h\nu$  from the radiation and its energy on emerging from the atom will be  $h\nu - w_K$ . Similar effects will occur at the other absorption levels in the radiating atom. Thus for incident radiation of definite frequency  $\nu$  the corpuscular radiation will contain groups of electrons the energies of which are  $h\nu - w_K$ ,  $h\nu - w_L$ , and so on. Thus if we measure these energies experimentally from the observed magnetic deflections, the energy values for the different levels in the radiating atom can be determined. The values obtained in this way are in excellent agreement with those determined by the methods already described. The method has the advantage that it can be applied to determine the energy associated with levels for which the critical absorption wave length is too great to be investigated by the absorption method, such for example as the  $K$  level for oxygen and the  $M$  and  $N$  levels for elements of medium and high atomic numbers.

These definite groups of electrons are always accompanied by a background of "general" corpuscular radiation, the velocity of which varies continuously up to a definite limit. This "general" corpuscular radiation appears to be associated with

the scattered X-radiation, and, like this, has not yet been accounted for satisfactorily by the quantum conditions which hold for the characteristic groups. The fastest electron emitted by a radiator of any substance has an amount of energy which is, within one or two per cent, that of the quantum of the shortest wave length present in the primary beam, and hence that of the fastest cathode particle in the X-ray tube from which this primary radiation comes. Thus an X-ray pulse after travelling for any distance from its point of origin is able to concentrate practically the whole of its energy on a single electron in the atom on which it falls. For observations of this kind the classical wave theory can offer no explanation.

**100 Ionization by X-rays.** The ionization of gases by X-rays has been frequently referred to, being the property usually employed to measure the intensity of the rays. The number of ions so formed is never more than an exceedingly small fraction of the total number of molecules subjected to the rays, even in the most favourable cases the proportion does not exceed one in  $10^{12}$ .

The degree of ionization produced by a given beam of X-rays depends on the nature of the gas and on its pressure. If the conditions are such that no homogeneous radiation is excited in the gas, the ionization is directly proportional to the pressure of the gas down to the lowest pressures at which measurements have been made. The relative amount of ionization produced in various gases at the same pressure depends upon the nature of the gas, and also to a smaller degree on the quality of the rays. In general it increases with the atomic weight of the gas. It is exceptionally small in hydrogen, the number of ions per unit volume for a given intensity of radiation being less than one per cent of that in air at the same temperature and pressure while the ionization in mercury methyl is no less than 425 times that in air under the same conditions.

Providing the density of the gas is kept constant the ionization produced in a gas under given conditions is independent of the temperature over a range of temperatures from  $-180^{\circ}\text{C.}$  to  $+180^{\circ}\text{C.}$

In all experiments on ionization of gases by X-rays it is most important to avoid exciting the corpuscular radiation from the electrodes or the walls of the ionization chamber, as the ionization produced by these rays is sufficiently large to mask almost completely the ionization produced by the direct action of the beam on the gas. The form of ionization chamber shewn in Fig 5 is convenient. The incident rays must be carefully limited by lead diaphragms so as not to strike the electrodes which are made of aluminum, in order to reduce as much as possible the effects which may be produced by the scattered radiation from the gas falling on them. The window admitting the rays and the far end of the chamber should be sufficiently far from the electrodes to ensure the complete absorption of the corpuscular radiation from them in the gas before reaching the neighbourhood of the electrodes. The electrode connected to the electroscope may be surrounded if desired by a wide guard ring, so that the electric field across the gas is straight and uniform. The number of ions formed in 1 c.c. of air under these conditions will be proportional to the energy absorbed by the air from the incident X-radiation. This principle has been employed to set up a unit of "dosage" for medical purposes. A "dose" of 1 e is said to have been given when the ions formed in 1 c.c. of air under standard conditions convey to the electrode a charge of 1 e.s.u. It is clearly a measure of the energy absorbed from the radiation.

X-rays ionize the gas, not directly but by means of the corpuscular radiation excited in the gas by the passage of the rays. These electrons as we have seen are emitted with a high velocity, and in passing through the gas produce ionization by collision with the molecules of it. Various indirect evidence of this has been accumulated. It is, however, proved directly by the photographs of the passage of a beam of X-rays through a gas taken by C. T. R. Wilson's expansion method (Fig 18). The tracks of the electrons emitted by the rays are shewn up clearly by the condensation of the water drops on the ions produced by them. The track of the beam of primary X-rays shews no such ions. It is only evident as the line from which the corpuscular tracks begin. Hence the X-rays produce no



ions directly, but only through the medium of the secondary electrons ejected by them from the atoms of the gas. It is also clear from the photograph (Fig. 18), which is taken in a gas at ordinary pressure, that only an exceedingly minute proportion of the atoms through which the rays pass eject an electron. This fact has found no explanation on the ordinary continuous wave front theory of radiation.

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## CHAPTER XI

### THE $\alpha$ -RAYS

101. **Properties and nature of the  $\alpha$ -rays** The  $\alpha$ -rays from radio-active substances are distinguishable from the other radiations by their absorbability, being completely stopped by less than 10 cm of air or 1/10 mm of aluminum. They can be detected by their action on a photographic plate, which is, however, very weak, by the ionization they produce in the gases through which they pass which is very intense, or by the fluorescence they produce on a fluorescent screen, the latter method being extremely convenient especially when the radiation is weak. On observing the fluorescence through a low power microscope it is found to consist of a succession of scintillations produced by the successive impact of the individual particles in the rays. It has been shown that each particle produces a separate flash on the screen when it collides with it. The impact of a single  $\alpha$ -particle can thus be observed.

With sensitive apparatus the ionization produced by a single  $\alpha$ -particle can also be detected, especially if the effect is multiplied by causing the ions originally produced to make fresh ions by collision. On account of the ease with which a single particle can be observed much more is known about the properties of the  $\alpha$ -particles than about those of the  $\beta$ -rays.

By passing a beam of the rays down a long exhausted tube and applying electric and magnetic fields it can be shown that the  $\alpha$ -rays consist of particles carrying a positive charge. The velocity of the particles and the value of the ratio  $e/m$  can be deduced from the deflections in the usual ways. The value of  $e/m$  is the same for all the  $\alpha$ -particles no matter what their source and is equal to 4823. The velocity depends on the radio-active substance from which they are ejected but is a constant for all the particles coming from the same sub-

stance. These velocities range from  $1.45 \times 10^9$  to  $2.2 \times 10^9$  cm. per sec.

**102. Nature of the  $\alpha$ -particle.** The ratio of charge to mass for a hydrogen atom when carrying a single electronic charge is 9647 e m u per gm. The value for an  $\alpha$ -particle is 4823 or half that of the hydrogen atom. If the charges were the same the particle would thus be twice the mass of the hydrogen atom, and hence probably a hydrogen molecule. It will be shewn later that the particle carries double the charge carried by an electron, its real mass is therefore four times that of a hydrogen atom, and thus corresponds very closely with that of the helium atom (atomic weight 3.96).

The proof of the identity of the particles with helium has been rendered complete by an experiment due to Rutherford. A very thin walled glass tube *A* (Fig. 81) was sealed into an outer tube *B* which was highly exhausted and connected to a small discharge tube *C*. To prove that there was no connection between *A* and *B* the former was filled with helium under pressure and left for some hours. No trace of the helium spectrum was obtained in the discharge tube *C*. The helium was carefully removed and radium emanation was passed into *A*, and allowed to stand. The glass walls of *A* were sufficiently thin to allow the  $\alpha$ -particles from the emanation to pass into *B* where they were stopped by the outer walls. Under these circumstances the helium spectrum became visible in *C* in a few hours, and became brighter as the experiment was continued. As the  $\alpha$ -rays were the only particles entering *B* during the experiment it is clear that the  $\alpha$ -particles must be atoms of helium.

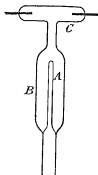


Fig. 81

**103 Determination of the charge on an  $\alpha$ -particle.** Let *N* be the number of  $\alpha$ -particles given out per second by a point source of rays. The number falling on a surface subtending a solid angle  $\Omega$  at the source will be  $\frac{\Omega}{4\pi} N$ , assuming that the

particles are given off equally in all directions. If  $E$  is the charge on each particle the total charge reaching the area per second will be  $\frac{\Omega}{4\pi} EN$ . Thus if we can determine this charge and the value of  $N$  we can deduce  $E$ .

The experiments were first performed by Regener. The number of  $\alpha$ -particles striking a given area per second was determined by counting the scintillations they produced on a fluorescent screen of brown diamond, of known area placed at a known distance from the radio-active material. The charge carried by the rays was found by allowing them to enter a

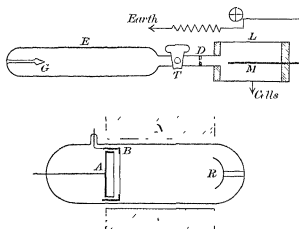


Fig 82

Faraday cylinder. In this way Regener obtained a value for the charge on an  $\alpha$ -particle of  $9.58 \times 10^{-10} \text{ esu}$ .

Owing to the uncertainty which existed at the time as to whether every  $\alpha$ -particle produced a scintillation on striking a fluorescent screen, the experiments were repeated by Rutherford, using an ionization method. Rutherford's apparatus is shown in Fig 82.

The detector consisted of a cylindrical ionization chamber  $L$  with a central wire electrode  $M$ , the rays entering the chamber through a stop  $D$  of known aperture. The central wire was connected to an electrometer, while the outer case was connected

to a battery of cells. The pressure in  $L$  was reduced until the field applied was sufficient to produce a considerable degree of ionization by collision in the remaining gas. Thus when a supply of ions was created in the gas by the entrance of an  $\alpha$ -particle the effect was multiplied by collision and a considerable charge reached the electrometer, the needle of which gave a considerable deflection. Thus the entrance of a single particle was signalized by a kick in the electrometer needle. As it was not desirable to let these charges accumulate, the electrometer quadrant was placed to earth through a very high resistance, so that the charges leaked away to earth.

The source of rays was radium C (§ 135) which was concentrated on a metal cone  $G$ . The distance  $GD$  being known (about 150 cm.) the solid angle subtended by the aperture at the source  $G$  could be calculated. From the number of particles actually entering the chamber through the aperture the whole number emitted per second could be calculated. When desired the particles could be prevented from entering  $L$  by turning the tap  $T$  as shewn in the diagram so as to close the passage. It was found that the number of particles emitted per gm. of radium C per second was  $3.4 \times 10^{10}$ .

The charge emitted per second by the same product was measured by allowing the rays to fall on a thick plate  $A$  connected to a sensitive electrometer. The radium C was deposited at the bottom of a shallow cup  $R$ , and the area of the aperture  $B$  and its distance from  $R$  were accurately known. In order to avoid any loss of charge from  $A$  by ionization currents the apparatus was exhausted to a very high vacuum. When  $\alpha$ -rays impinge on matter they give rise to a considerable emission of very slowly moving negative corpuscles often known as  $\delta$ -rays. If these were allowed to leave the disc  $A$ , or to reach it from other parts of the apparatus struck by the rays, a considerable error would arise. To prevent this the whole apparatus was placed between the poles of a strong electromagnet  $NS$ , which by curling the paths of the  $\delta$ -rays into very small circles prevents them from leaving their point of origin. Very thin aluminium leaf placed across the opening  $B$  and across the entrance to  $A$  serves a similar purpose.

In this way it was calculated that one gram of radium C would give out 31.6 electrostatic units of positive charge per second.

The number of carriers was, as we have seen,  $3.4 \times 10^{10}$  per second, and thus the charge on each  $\alpha$ -particle is  $9.3 \times 10^{-10}$  e.s.u. Regener obtained a value  $9.58 \times 10^{-10}$  e.s.u. using a polonium disk. It will be seen that the mean of these numbers is almost exactly twice the value  $4.77 \times 10^{-10}$  which we have seen represents the best value for the charge on an electron. Thus the charge on an  $\alpha$ -particle is twice the charge on an electron, and the  $\alpha$ -particle is an atom of helium which has lost two electrons. The close agreement of the numbers obtained in this way with those previously obtained by experiments on negative electrons is a further proof of the atomic nature of electricity. Their mutual agreement proves the truth of the assumption made by Regener that each  $\alpha$ -particle produces a separate scintillation on a suitable fluorescent screen.

**104 Passage of the  $\alpha$ -rays through matter.** It has been noted that the  $\alpha$ -rays are completely stopped in a very small thickness of matter. If a layer of radio-active material is deposited on a plate and successive thin sheets of, say, aluminium leaf are placed over the layer the activity of the rays passing through is gradually reduced. The method, however, is not a good one. The  $\alpha$ -rays are emitted in all directions and the path of the oblique rays in the absorbing sheet will be much greater than that of the rays which are projected normally to the surface. The effects are, therefore, complex, and the absorption curve under these circumstances is approximately exponential. In order to study the subject in detail it is necessary to work with pencils of the rays of small angle so that the paths of the different particles are approximately parallel to each other. This can most easily be effected by taking a point source of radiation and limiting the rays by means of a small aperture in a lead plate at some little distance from the source.

If such a pencil is allowed to fall on a fluorescent screen the number of particles falling on the screen can be measured by counting the scintillations. If now very thin sheets of some

absorbing substance are interposed between the aperture and the screen, it is found that the number of scintillations made per second on the screen remains constant until the thickness of absorbing material reaches a certain critical value (depending on the nature of the absorbing substance and the velocity of the rays) at which the scintillations suddenly cease. There is thus for each substance a definite thickness which the rays can penetrate, all the particles making up the rays penetrating to exactly the same distance. This critical distance is called the *range of the particles* in the substance.

The range depends only on the velocity of the particles and the nature of the absorbing substance. It is of course necessary in these experiments to work with a very thin layer of radio-active substance. All the particles are initially projected from the same radio-active substance with the same velocity. If, however, the emitting layer is thick the particles from the deeper portions of it will have completed part of their course before reaching the surface, and their range in the air or other absorbing medium above will be correspondingly reduced.

As the absorption in solids is very large, the range is generally measured in air at atmospheric pressure. Under these circumstances the range of the  $\alpha$ -particles from radium C is 7.0 cm, and those from radium itself 3.5 cm. The range in a given substance depends only on the mass of matter traversed by the rays. In a gas it is thus inversely proportional to the pressure. This fact is made the basis of a very simple method of finding the range of an  $\alpha$ -particle. The radio-active matter is placed at the centre of a spherical flask, the walls of which are coated inside with willemite or other fluorescent substance. The flask is then gradually exhausted until the  $\alpha$ -particles can just reach the walls of the flask and scintillations begin to appear. The range at atmospheric pressure is then the radius of the sphere multiplied by the ratio of the atmospheric pressure to the actual pressure in the flask.

The absorption of the  $\alpha$ -rays is thus not due to a gradual diminution of their number, as this number remains constant until the rays completely disappear. It must consequently be due to a gradual absorption of their energy. The matter has

been tested directly by measuring the velocity of the particles after passing through various absorbing sheets of matter. The experiments are made particularly easy by the use of the fluorescent screen. The rays from a wire  $R$  excited by exposure to radium emanation pass down a long exhausted glass tube  $T$  (Fig. 83) and are formed into a narrow pencil by the lead diaphragm  $D$ . This beam then continues between the poles of an electromagnet  $NS$ , and falls on a screen  $F$ . From the geometry of the apparatus and a measurement of the shift produced in the fluorescent spot when the magnetic field is turned on the radius of curvature of the rays in the magnetic field can be calculated, and using the equation  $\rho = vm/He$  (37)  $v$  can be calculated since the ratio of  $e/m$  for the rays is known. It was found that the velocity of the rays after passing through a distance  $x$  of air could be expressed in the form

$$v^3 = a(R - x) \quad . \quad . \quad (94)$$

where  $R$  is the range of the particle in air. The cube of the

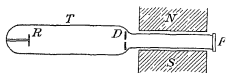


Fig. 83

velocity is thus directly proportional to the distance the ray has still to run. The absorption is thus an absorption of the energy of the particles during their passage through matter. This conclusion has been confirmed by direct experiment by Kapitza who has measured the natural energy of the rays at different points along their course, by absorbing them in a silver disk, and measuring the heat developed by a sensitive radio-micrometer.

A portion at any rate of this absorbed energy is used in ionizing the gas. It is a probable assumption, which is confirmed by the experiments of Kapitza referred to above, that the ionization produced by an  $\alpha$ -ray in a given thickness of matter is propor-



tional to the energy absorbed. On this assumption the intensity of the ionization  $I$  will be proportional to  $\frac{d}{dx}(\frac{1}{2}mv^2)$  or since the mass is constant

$$I \propto \frac{d(v^2)}{dx} \propto \frac{d}{dx}(R-x)^{\frac{1}{2}} \\ \propto (R-x)^{-\frac{1}{2}}, \\ I^2 = a'/(R-x) \quad . \quad . \quad . \quad (95)$$

where  $a'$  is a constant

According to this expression the ionization produced by an  $\alpha$ -particle should increase as the velocity decreased, rising to a very sharp maximum as the particle reaches the end of its range and then immediately dropping to zero when the particle comes to rest

It will be noticed that combining the two equations we have

$$Iv = \text{constant} \quad . \quad . \quad . \quad (96)$$

The amount of ionization produced in an atom by an  $\alpha$ -particle is thus proportional to the time which the particle takes to pass across an atom, a very interesting result.

**105. Bragg's experiments on the range of the  $\alpha$ -particles**  
The measurement of the ionization produced by  $\alpha$ -rays at various points along their path was investigated by W. H. Bragg (3), whose experiments (which were considerably earlier than those we have just described) were the first to throw light on the absorption of the rays. His apparatus is shown very diagrammatically in Fig. 84 (a) and in rather more detail in Fig. 84 (b). The  $\alpha$ -rays originate in a very thin film of radio-active substance at  $R$  and are limited to a fine pencil by the lead stop  $C$ . The ionization chamber consists of two plates  $A$  and  $B$  very close together, the lower one being made of gauze to allow the entrance of the rays. The saturation current between the electrodes is proportional to the mean intensity of ionization between  $A$  and  $B$ . By altering the distance between the ionization chamber and  $R$  the ionization produced by the particles at various points on their path can be measured.

The ionization produced in such a narrow chamber by such a small pencil is very small. The effect is increased therefore

by forming what is practically a series of such arrangements side by side. The radio-active substance is deposited in a very thin layer over the plate  $R$  (Fig 84(b)), which is then covered with a grid  $T$  formed of a large number of metal tubes placed side by side. It is found more convenient to move the radio-active matter rather than the ionization chamber, so that  $R$  is carried by a rod  $L$  which can be raised or lowered by a micrometer screw. The distance of  $R$  from the ionization chamber can thus be accurately measured. In order that different gases and different pressures could be employed the apparatus was enclosed in an air-tight case.

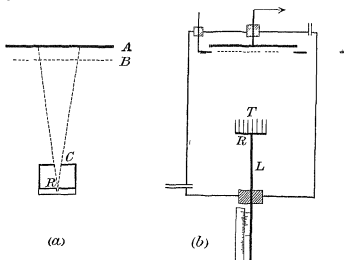


Fig 84

Using a single radio-active substance, such as radium C, Biagg obtained a curve similar to that in Fig 85. The ionization produced increases with the distance from the source up to a maximum and then drops with great rapidity to zero. The agreement with the theoretical curve shown by the dotted lines in the same diagram is thus sufficiently close. The fact that the cessation of ionization is not quite abrupt is due to two causes. In the first place the beam used is not accurately parallel, so that the normal rays penetrate to a somewhat greater distance from the source than those which are more

oblique before traversing the same actual distance in the gas. In the second place some of the rays are deviated by collision with the particles of air and hence even if the beam were originally parallel some of the particles would become oblique

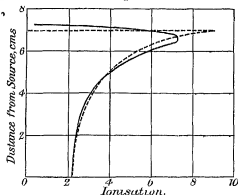


Fig 85

before reaching the end of their path and would thus not travel the full vertical distance from the source. We shall return to this point later.

The ionization per cm of path depends only on the speed of the  $\alpha$ -particle. Thus, if the curve is drawn for the  $\alpha$ -particles from radium itself, the rays from which have only half the range of those from radium C, it will be found to be the same as that for radium C but with each ordinate decreased by a constant amount equal to the difference between the ranges of the two sets of particles. The relation between the curves for the two sets of rays is represented by the two curves in Fig 86.

In his earliest experiments Bragg used a thin layer of ordinary radium and obtained a complex curve shown by the

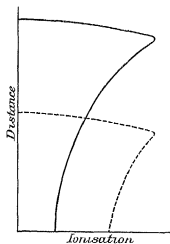


Fig 86

thick line in Fig 87. We are now in a position to consider this curve.

It has been shewn that a sample of radium which has been standing for some time is really a mixture of several radio-active substances, namely radium itself, its emanation, and radium A, B and C (Chap XIV). Of the five substances present, radium B emits only  $\beta$ - and  $\gamma$ -rays. We are thus left with four  $\alpha$ -ray producing substances, and four sets

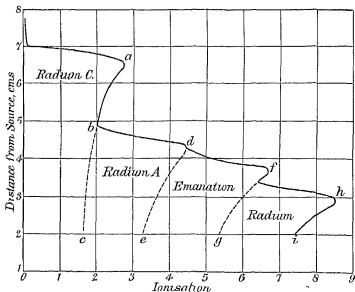


Fig 87

of  $\alpha$ -rays. Their ranges in air at normal pressure are 3.50, 4.23, 4.83, and 7.06 cm respectively.

Let us commence by drawing the curve for the  $\alpha$ -particles from radium C, which have the longest range. It is represented by the line *Oabc* on Fig 87. The *abscissa* of this curve represents the total ionisation at the distance of the corresponding *ordinate* due to the rays from radium C. Now by Rutherford's theory of radio-active equilibrium (§ 126) the number of atoms of each product which are transformed in each second must be the same for each product, since for

equilibrium the quantity of radium emanation, say, which is changed into radium A must equal the amount of emanation formed from the radium in the same time, and hence the amount of radium decomposed. Hence if each atom is disintegrated with the emission of one  $\alpha$ -particle, the number of  $\alpha$ -particles from each of the products must be the same. To obtain the curve for radium A we have to lower each of the ordinates of the radium C curve by 2.23 cm. the difference in range between the two sets of particles. The sum of the abscissae of these two curves will give the ionization due to the  $\alpha$ -particles from the radium C and radium A, in the substance. In an exactly similar way we can obtain the curves for the emanation and radium itself since all the ranges are known. The sum of these abscissae at any point will give the total ionization to be expected at a distance from the source given by the corresponding ordinate. In this way we can build up the full curve *Oabdfhi* (Fig. 87). The curve so obtained is found to agree exactly with the experimental curves obtained by Bragg for radium in radio-active equilibrium with its products.

This agreement affords an excellent proof of the two assumptions we have made (*a*) that allowing for the difference in velocity of projection the ionization curves are the same for radium and each of its products, (*b*) that with radium in radio-active equilibrium, the number of  $\alpha$ -particles projected per second from each product is the same. This affords very strong confirmatory evidence of the truth of Rutherford's theory of radio-active change which is described more fully in a subsequent chapter (Chap. XIII).

**106 The stopping power of an atom for  $\alpha$ -particles.** If the source of  $\alpha$ -rays is covered with a thin sheet of metal, the effect is to reduce the velocity of the particles and thus to reduce each ordinate of the distance-ionization curve (Fig. 85) by a definite amount. By measuring the distance through which the maximum of the curve is lowered, that is, the reduction of the range of the particle, we can calculate the quantity of an at normal pressure and temperature to which the given sheet is equivalent. In a compound curve such as that of Fig. 87

each ordinate is reduced by exactly the same amount. Experiments on these lines using leaf of different materials enable us to find the equivalent thickness of air for various substances. It is obvious that for a given substance it is the mass per unit area and not the thickness of it on which the reduction in velocity depends.

The ratio of the mass of a column of air of unit cross section to the mass per unit area of the substance which produces the same diminution in the speed of the  $\alpha$ -particle is called the *stopping power* of the substance.

It was found better to express the stopping power in terms of the number of atoms traversed rather than in terms of the mass. The transformation can easily be made. Thus the stopping power of silver is 0.415, that is to say, in passing through a given mass of silver the velocity of the  $\alpha$ -particle is only reduced by 0.415 of the decrease produced in passing through an equal mass of air. But for equal masses of air and silver the former contains  $108/14.4$  times the number of atoms, hence atom for atom silver stops  $0.415 \times \frac{108}{14.4} = 3.1$  times as much as air. This is called the *stopping power of the atom*. Experiment has shewn that except in the case of very light elements *the stopping power per atom is proportional to the square root of the atomic weight*, the mean value of the stopping power over the root of the atomic weight being about 0.3.

The stopping power of an atom is independent of its state of chemical combination, being the same in compounds as in the free state. Thus the stopping power of a compound can be calculated from that of its constituents.

107 **The scattering of the  $\alpha$ -particles** We have so far tacitly assumed that the  $\alpha$ -particles travel in straight lines through the gas, and the agreement observed between theory and experiment shews that this assumption is true in the main. There is, however, always the possibility that a collision between an  $\alpha$ -particle and a molecule may produce a deflection of the former. In this case although the actual length of path of the particle might remain the same it would not penetrate so

far from the point of origin. Thus taking a bundle of rays, the ionization between the plates (§ 105) would fall off somewhat less abruptly than would be the case if the particles suffered no deflection. This is illustrated in Fig. 88, where  $e$ ,  $f$  and  $g$  are supposed to represent the actual paths of three  $\alpha$ -particles of equal range, two of which suffer deviation from their course before reaching the ionization chamber  $AB$ . Such a deviation is to be seen in the case of one of the actual tracks of  $\alpha$ -particles shewn in Fig. 16.

The scattering of the  $\alpha$ -rays has been investigated by Geiger using the fluorescent screen method, which is specially convenient for experiments of this kind as it enables us to detect individual particles. He found that in many cases the individual particles suffered appreciable deflections from their initial directions, before reaching the end of their course. The deflections were, as might be expected, distributed according to the probability law. In passing through a thickness of gold leaf equivalent in stopping power to 3.68 cm. of air the average deflection was as much as  $7^\circ$ . The most probable angle was roughly proportional to the thickness of material through which the rays had passed.

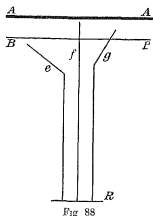


Fig. 88

Occasional particles were, of course, in accordance with the law of probability deflected through much larger angles. Using a gold plate it was found that one particle in about 8000 suffered a deflection greater than  $180^\circ$  and so emerged on the side on which it had entered. These results sufficiently explain the want of abruptness in the ending of the curve of Fig. 85.

As might be expected the deviations are most violent where the velocity is smallest, that is, near the end of the path.

Having lost its velocity the  $\alpha$ -particle is no longer able either to ionize or to produce scintillations on a screen. It is also unable

to retain its charge, and thus becomes simply an atom of helium subject to the ordinary laws governing a gaseous particle

So far we have been considering only the effect of the collision on the  $\alpha$ -particle itself. It is obvious, however, from the ordinary laws of impact, that if the atom with which it collides is free to move the atom itself will be projected as the result of the impact, with a velocity which may be comparable with that of the  $\alpha$ -particle itself, or, if the atom is lighter than the  $\alpha$ -particle, may even exceed that velocity. Suppose, for example, that an  $\alpha$ -particle makes a direct, or "head on" collision with an atom of hydrogen. If the forces between the two are electrical only, and due to the mutual repulsion of their charges, the collision will be perfectly elastic and the velocity  $v$  of the hydrogen atom after collision will be given by

$$v = \frac{2M}{m + M} V,$$

where  $m$  and  $M$  are the masses of the hydrogen atom and the  $\alpha$ -particle, and  $V$  the velocity of the latter. Thus  $v = 1.6V$ . If we assume that the range of the particles is proportional to the cube of the velocity, the range of the projected hydrogen atom should be  $(1.6)^3$  or four times that of the original  $\alpha$ -particle. We should expect, therefore, on fixing a beam of  $\alpha$ -particles through a column of hydrogen that occasional scintillations would be observable far beyond the normal range of the  $\alpha$ -particles in the gas. These conclusions have been verified by Marsden. A narrow pencil of  $\alpha$ -particles was passed down a tube containing hydrogen and allowed to fall on a fluorescent screen. The range of the  $\alpha$ -particles used was 24 cm. in hydrogen, and the majority of the scintillations disappeared abruptly when the length of the column through which the rays had to pass was increased to this value. Occasional scintillations however continued to be observed up to a distance of 82 cm., that is to say, some of the hydrogen atoms had acquired a velocity, as the result of the impact of an  $\alpha$ -particle, sufficient to give them a range of nearly four times that of the  $\alpha$ -particles themselves. This agrees sufficiently closely with the calculation just made.



Assuming then that the deflections of the  $\alpha$ -particles are due to the mutual repulsion of the positive charge on the particle and the positive charge of the atom, each of these charges must be concentrated in a space which is small compared with the volume of an atom. To produce a force capable of giving to the swifter hydrogen atoms the velocities actually attained it can easily be shewn that the positive charges must approach within a distance less than  $3.5 \times 10^{-13}$  cm. assuming that they act like point charges up to this distance. Assuming that the positive charge in an atom is concentrated on a nucleus of this order of magnitude the determination of the deflection of an  $\alpha$ -particle by a fixed atom reduces to the problem of calculating the orbit of a particle moving with a known velocity in the neighbourhood of a fixed particle which repels it with a force which varies inversely as the square of the distance, a problem of which the solution is given in books on Mechanics. The path of the moving particle is a hyperbola, with the fixed particle at the focus, and the deflection is measured by the angle between the asymptotes. If the perpendicular distance of the fixed particle from the original path of the moving particle is  $p$  it is shewn in treatises on Mechanics that

$$p = \frac{E_1 E_2}{2T} \cot \frac{\phi}{2},$$

where  $E_1$  and  $E_2$  are the charges on the particles,  $T$  is the kinetic energy of the moving particle and  $\phi$  the deflection produced. Now the probability that the path of an  $\alpha$ -particle will pass within a distance  $p$  of the centre of an atom is proportional to  $\pi p^2$  for a single atom, or if we have a sheet of substance of thickness  $l$  and containing  $n$  atoms per unit volume, the probability that the particle will approach within a distance  $p$  of one of them, and thus experience a deflection greater than the corresponding value of  $\phi$ , is  $\pi p^2 n l$ . But, when dealing with a large number of particles, the probability that the deflection is greater than  $\phi$  is obviously equal to the fraction of the particles which are deflected through an angle greater than  $\phi$ . This is a quantity which can be determined by direct experiment. If we call it  $\rho$  we have

$$\rho = \pi n l \left( \frac{E_1 E_2}{2T} \right)^2 \cot^2 \frac{\phi}{2}$$

The charge on an  $\alpha$ -particle is  $2e$ , where  $e$  is the electronic charge. If the charge on the fixed nucleus is  $Ne$  then

$$\rho = \pi m t \frac{N^2 e^4}{T^2} \cot^2 \frac{\phi}{2}.$$

We have neglected, in making these calculations, the effect of the negative electrons which are also present in the atom. We have also neglected the possibility that a single  $\alpha$ -particle may be deflected by more than one atom. Rutherford(4), to whom the theory is due, was able to shew that at any rate for thin sheets of material, such as are used for experiments on the scattering of  $\alpha$ -particles, and for all elements except those of very low atomic weight both these effects are negligible.

Experiments on these lines have recently been carried out by Chadwick(5) with considerable accuracy. The source of the  $\alpha$ -particles was placed at  $A$  on the axis of a brass plate in which had been cut a narrow circular zone  $PP$ . The scattering substance (very thin leaves of copper, silver, or gold) covered this clear zone, while the observing screen was placed, also on the axis of the plate, at  $S$ . The apparatus can be visualized from the section in Fig. 89 by imagining the diagram to be rotated about the axis  $AS$ . Thus the only particles which could fall on the screen at  $S$

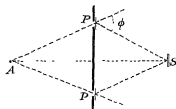


Fig. 89

were those which had been scattered through an angle  $\phi$  during their passage through the leaf. By varying the position of the plate this angle could be varied. It was found that, for all the angles employed, the relation between  $\phi$  and the number of particles falling per second on the screen was that indicated by the theory. Thus for such collisions the assumption that the particles behave like point charges is justified. The closest approach of the two centres in these experiments was of the order of  $10^{-12}$  cm. It was further found that for the three substances used the value of  $N$  as calculated from the theory was equal to the atomic number of the scattering substance to an

accuracy of at least 1 per cent. The resultant positive charge on the nucleus of an atom, measured in "electronic" units, is thus exactly equal to its atomic number. This result is of great importance, as the method is by far the most direct for determining the charge on the atomic nucleus.

**108 The collision of  $\alpha$ -particles with atoms** The experiments just described indicate that at distances greater than  $10^{-12}$  cm. the positive charges on the atoms may be regarded as point charges obeying the inverse square law of force. For direct collisions, however, especially with the fastest  $\alpha$ -particles, the closest distance of approach may, as we have already seen, be considerably less than this. Experiments made by Rutherford (6) on the collision of these particles with hydrogen indicate that for these closer impacts the law no longer holds.

The  $\alpha$ -particles in their course through the gas will pass the hydrogen atoms at varying distances from their centres, and will thus make collisions which will vary in obliquity. Thus, on the assumption that they behave as point charges, they will set the hydrogen atoms in motion at angles varying from  $0^\circ$  to  $90^\circ$  with their own direction. If thin sheets of absorbing material are interposed in the path of these hydrogen rays the relation between the thickness of material and the number of particles transmitted should be similar to that for the  $\alpha$ -particles from an extended source (§ 104). That is to say it should be approximately exponential owing to the varying obliquity of the paths in the substance. When the experiments were made with  $\alpha$ -particles of moderate velocity, say of 6 cm. range or less, this was found to be the case. With faster  $\alpha$ -particles, however, quite a different relation was obtained. In fact, using particles of 7 cm. range from radium C, the number of hydrogen particles transmitted by the absorbing substance was independent of the thickness over the first three-quarters of the whole range, and only then began to fall towards zero. The relation is in fact almost identical with that obtained for a parallel pencil of  $\alpha$ -rays (§ 104). Thus, instead of the hydrogen atoms being projected in all directions, the majority of them must have been given velocities very nearly parallel to that of the  $\alpha$ -particles themselves. At

these very close impacts, therefore, the inverse square law breaks down

The type of collision actually found with these high speed particles might be imitated mechanically by projecting through the gas a number of flat discs, or oblate spheroids, with their greatest area of cross section at right angles to the direction of motion. A careful measurement of the actual distribution of directions among the projected hydrogen atoms has been made by Chadwick and Bieler<sup>(7)</sup>. The distribution actually found is that which would be produced by mechanical collision with oblate spheroids having semi-axes of about  $8 \times 10^{-13}$  and  $4 \times 10^{-13}$  cm. This mechanical analogy cannot be pressed too far. The results indicate, however, that the  $\alpha$ -particle has an extension which must be taken into account at distances appreciably less than  $10^{-12}$  cm. and that its structure is asymmetrical.

On repeating his experiments in an atmosphere of nitrogen instead of hydrogen, Rutherford<sup>(8)</sup> found that scintillations could again be observed far beyond the normal range of the  $\alpha$ -particles employed. In fact the range of these particles from nitrogen was identical with that of the particles projected in hydrogen (28 cm. in air). An examination of these particles by the method of magnetic deflection confirmed what had originally been suggested by their range, that they were atoms of hydrogen, or rather, since they are positively charged, hydrogen nuclei. The only possible interpretation of these results is that the forces called into play in the collision between the  $\alpha$ -particles from radium C and the nitrogen atom are sufficient to cause a disruption of the latter structure. Similar particles are also produced when these swift  $\alpha$ -particles are projected through aluminium, boron, sodium, phosphorus, and other light elements<sup>(9)</sup>. The particles are projected not only in the forward, but also in the backward direction, their velocity in the backward direction being, however, somewhat less than in the forward direction. A careful measurement of the velocities of these particles indicates that for most of the substances concerned the disintegration results in an actual liberation of energy, amounting for aluminium to as much as 42 per cent. of that of the

original  $\alpha$ -particle. These long-range hydrogen particles are producible from all the elements of odd atomic number at any rate as far as potassium. They are not observed with the elements of even atomic number. A modification of the experiment which enables observations to be made within the actual range of the  $\alpha$ -particles employed for the experiments, has revealed the production from elements of even atomic number of particles of much smaller range, and hence smaller velocities, than the long-range hydrogen nuclei already dealt with. It is suggested that, in some cases, these may be helium nuclei.

It may also be observed that the atomic masses of the elements yielding the long-range particles can all be expressed by  $4n + 3$ , or, in the case of nitrogen,  $4n + 2$ , where  $n$  is an integer. They are not produced from elements such as carbon or oxygen, whose atomic weights are exact multiples of 4. This suggests that the positive particles of which the atomic nucleus is constructed and which are presumably hydrogen nuclei tend to arrange themselves into very stable groups of four. This group of four (which of course corresponds to the nucleus of a helium atom) is not disintegrated by the impact of the  $\alpha$ -particle. The long range particles which are emitted, are the particles which are left over after the formation of the stable groups, and Rutherford suggests that these extra particles may be regarded as revolving like satellites around the stable groups. These results are of great interest, and throw much new light on the problem of atomic structure.

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## CHAPTER XII

### THE $\beta$ - AND $\gamma$ -RADIATIONS

**109 Nature of the  $\beta$ -rays** The  $\beta$ -rays can be distinguished from the  $\alpha$ -rays by their greater penetrating power, as they are able to produce measurable effects after passing through absorbing sheets of 100 times the thickness required to stop the  $\alpha$ -particles. Their nature was first investigated by Becquerel who shewed that they consisted of charged particles by the following simple experiment. A small quantity of uranium oxide was placed in a small lead dish on the back of a photographic plate, the film side being downward. The whole was then placed between the poles of an electromagnet in a dark room. After some hours the plate was developed, and was found to be blackened immediately below the lead dish, the paths of the rays having been bent into circles by the action of the field.

A modification of the same experiment (Fig. 90) shewed that the rays were heterogeneous. The plate was placed film side upwards between the poles of the magnet and exposed to the rays for some time. On developing the plate a diffuse

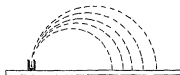


Fig. 90

patch was found shewing that some of the rays had been bent into smaller circles than others. By placing different thicknesses of aluminum foil on the plate it was found that the part of the patch nearest the source disappeared sooner than that further away. The more deviable rays were thus more absorbable than the others. Since

$$\rho = mv/He$$

these rays are the slower ones, assuming that the ratio of  $e/m$  is constant.

The similarity of the  $\beta$ -rays to cathode rays was further

established by Curie, who shewed that they carried a negative charge. In performing this experiment it is necessary to avoid the presence of air, as the latter becomes conducting under the action of the rays and the charge is thus unable to accumulate. In recent experiments this difficulty is overcome by working in a high vacuum. Curie however surrounded his plate by a solid dielectric instead. His apparatus is shown in Fig. 91.

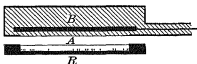


Fig. 91

The  $\beta$ -rays from the radio-active material in  $R$  penetrate the thin aluminum leaf  $A$  and the thin layer of wax, but are stopped by the lead plate  $B$ , giving up their charge to it. On performing the experiment it was found that the electrometer connected to  $B$  shewed a gradual but steadily increasing deflection when the source of radio-active substance was placed below  $A$ . The sign of the charge was negative.

**110 Determination of  $e/m$  and  $v$  for the  $\beta$ -rays** Since the  $\beta$ -rays are rapidly moving negatively charged particles we can apply to them the methods of measuring the ratio of the mass to the charge, and the velocity, which were employed for the cathode rays. The first accurate experiments were made by Kaufmann, they have been repeated by numerous observers.

The method adopted was the one where the electric and magnetic fields are parallel, and the two deflections thus at right angles to each other, the theory of which has already been considered (§ 54) in connection with the positive rays. The apparatus used is shewn in Fig. 92 (a).

The source of the rays was a small speck of radium compound placed at  $R$ , while the rays were limited to a narrow pencil by a slit  $A$  in a thick lead plate. Before reaching the hole  $A$  the rays passed between two metal plates, which could be adjusted by levelling screws to be perfectly parallel. The plates could

be raised to different potentials by means of wires which were fused through the walls of the containing glass vessel. The photographic plate  $P$  was mounted at the top of the chamber, and the whole was carefully exhausted to a very high vacuum. The whole vessel was placed between the poles of a strong electromagnet  $N, S$ .

On developing the plate the trace of the rays was a single continuous curved line (Fig 92 (b)). If the rays had differed only in velocity this curve would have been a parabola (see (50), § 54). The line, however, was not parabolic, shewing that the value of  $e/m$  was not constant but varied with the velocity. The fact that the line was single and unbroken shewed that this important

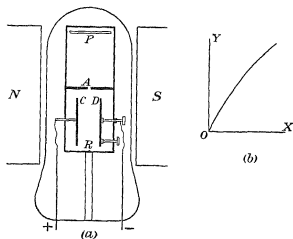


Fig 92

ratio was a continuous function of the velocity of the rays. In other words for every value of the velocity there was a single, definite value for the ratio  $e/m$  which depended on the velocity alone.

The calculations necessary to evaluate the results are hardly so simple as those for Sir J. J. Thomson's experiments on the positive particles. Allowance has to be made for the fact that the two fields are not coterminous. Very careful experiments and elaborate calculations were made to determine the end-corrections for the two fields.



Since the curve shewed no signs of breaks it was very improbable that the rays consisted of sets of different particles. It is equally improbable that the charge was gradually changing, since the great accumulation of evidence has shewn that the charge  $e$  is atomic. We are thus led to the conclusion that the mass of a  $\beta$ -particle is a function of the velocity with which it is moving.

**111 Electromagnetic mass** It can easily be shewn that a moving charge will act as if it possessed mass from the mere fact that it carries a charge. Consider a point charge moving with a velocity  $v$ . This will be equivalent to a current element coinciding with the path of the particle and equal to  $ev$ , where  $e$  is the charge and  $v$  the velocity. The magnetic field due to the moving charge at a distance  $r$  from it in a direction making an angle  $\theta$  with the direction of motion will thus be  $\frac{ev \sin \theta}{r^2}$ .

The energy in a magnetic field of strength  $H$  is  $\frac{\mu H^2}{8\pi}$  per unit volume. Hence if  $du$  is a small element of volume at the point considered the magnetic energy in that element of volume will be  $\frac{\mu}{8\pi} \left( \frac{ev \sin \theta}{r^2} \right)^2 du$ .

The whole magnetic energy in the space round the particle will be the integral of this from the surface of the particle to infinity. To evaluate this, with the electron as centre describe two spheres of radii  $r$  and  $r + dr$  and draw two radii making angles  $\theta$  and  $\theta + d\theta$  with the direction of motion. If these are supposed to rotate about the direction of motion of the electron they will cut out from the spherical shell an annulus the volume of which is

$$2\pi r \sin \theta \cdot r d\theta \cdot dr.$$

But the magnetic field is obviously constant throughout the space so obtained and hence the energy in the annulus is

$$\frac{\mu}{8\pi} \left( \frac{e^2 v^2 \sin^2 \theta}{r^4} \right) 2\pi r^2 \sin \theta d\theta dr = \frac{\mu e^2 v^2 \sin^3 \theta d\theta dr}{4r^2}.$$

The energy in the spherical shell is thus

$$2 \int_0^{\pi} \left[ \frac{\mu e^2 v^2 \sin^3 \theta}{4r^2} d\theta \right] d\theta = \frac{\mu e^2 v^2}{2r^2} \int_0^{\pi} \sin^3 \theta d\theta \\ = \frac{1}{3} \frac{\mu e^2 v^2}{r^2} dl. \quad (97)$$

If the charge is carried by a small sphere of radius  $a$  the total magnetic energy in the space is

$$\int_a^{\infty} \frac{\mu e^2 v^2}{3r^2} dr \\ = \frac{\mu e^2 v^2}{3a}. \quad (98)$$

This energy must be given to the particle when it is set in motion. If the particle has a mechanical mass of  $M$  the work done in giving the particle a velocity  $v$  is thus

$$\frac{1}{2} Mv^2 + \frac{\mu e^2 v^2}{3a} = \frac{1}{2} \left( M + \frac{2}{3} \frac{\mu e^2}{a} \right) v^2. \quad (99)$$

The particle thus behaves as if its mass had been increased by  $\frac{2}{3} \frac{\mu e^2}{a}$ . Thus even if  $M$  is zero the particle will have a mass equal to  $\frac{2}{3} \frac{\mu e^2}{a}$  due to its charge  $e$ , this is called its *electromagnetic mass*.

It can be shown on the electromagnetic theory that the above analysis is only true if the velocity of the particle is small compared with that of light (practically if it is less than one-tenth that of light). If the velocity of the particle approximates to that of light the distribution of the electric field round the moving charge is altered in such a way as to increase the electromagnetic energy of the field, and thus the electromagnetic mass of the particle. The analysis is complicated and starting from different assumptions as to the behaviour of the electron somewhat different formulae have been developed by different physicists. The various formulae differ very little from each other when translated into numbers, and it has been a matter requiring much experimental skill to distinguish between them.

Kaufmann adopted the formula of Abraham who gave

$$\frac{m_v}{m_0} = \frac{3}{4\beta^2} \left( \frac{1+\beta^2}{2\beta} \log \frac{1+\beta}{1-\beta} - 1 \right) \quad (100)$$

where  $m_v$  and  $m_0$  are the electromagnetic masses of the charged particle when moving with a velocity  $v$  and with an infinitesimally small velocity respectively, and  $\beta$  is the ratio  $v/c$  where  $c$  is the velocity of light. Kaufmann found that within the limits of experimental error his results could be exactly represented by this formula. But this formula represents only the electromagnetic mass of the particle. If the particle has any mechanical mass  $M$ , this will presumably be independent of the velocity, and the total mass of the particle will vary less rapidly than the electromagnetic mass alone. This is not found to be the case. Hence we are led to conclude that the whole mass of the negative particles constituting the  $\beta$ -rays is electromagnetic in nature. Since the value of  $e/m$  for the slowly moving  $\beta$ -particles agrees exactly with that for electrons from other sources (Table III, § 51) the  $\beta$ -particle must be identified with the electron. Hence the mass of any electron is electromagnetic and is due simply to the charge which it possesses.

The formula (98) can be applied to give us a value for  $a$ , the radius of an electron. Since  $m$  the mass of an electron is  $8.9 \times 10^{-28}$  gm

$$8.9 \times 10^{-28} = \frac{2}{3} \frac{\mu e^2}{a}$$

and since  $\mu$  the magnetic permeability of a vacuum is unity and  $e$  is  $1.59 \times 10^{-20}$  c.m.u. the radius of an electron is  $1.9 \times 10^{-13}$  cm. or roughly one ten-thousandth of the radius of an atom<sup>†</sup>. The electron will therefore bear to the atom which contains it approximately the same proportions as those of a pea to a cathedral.

**112 Variation of the mass of an electron with velocity**  
**Bucherer's experiments** Owing to the progress of modern theory a much simpler relation between mass and velocity,

<sup>†</sup> On the Principle of Relativity, all mass, whether electrical or not, should vary with velocity according to the formula (101). If this principle is accepted, the calculation of the radius of an electron from its mass is invalidated. The most direct evidence for the size of an electron is then supplied by the experiments on the collision of  $\alpha$ -particles with atomic nuclei. The  $\alpha$ -particle contains two electrons, and four hydrogen nuclei, the latter being probably of negligible size, and behaves as if its dimensions were roughly  $4 \times 10^{-13}$  cm. by  $8 \times 10^{-13}$  cm. The radius of an electron, therefore, cannot differ much from the value derived on the electromagnetic theory.

obtained originally by Lorentz, has now replaced the early formula of Abraham, and is found to give a better agreement with the latest experimental results. Lorentz's formula gives

$$m_v = m_0 (1 - \beta^2)^{-\frac{1}{2}} \quad (101)$$

where  $\beta$  is the ratio of the velocity of the particle to the velocity of light and  $m_v$  and  $m_0$  have the same meaning as before. This formula has been experimentally tested by Bucherer(2) using a very ingenious method. The source of the  $\beta$ -radiation was a small speck of radium fluoride  $R$  placed at the centre of two parallel plates  $A$  and  $B$  (Fig. 93) which were very close together. The plates were maintained at a considerable difference of potential, and the apparatus was placed in a uniform magnetic field at right angles to the plane of the paper. The  $\beta$ -particles

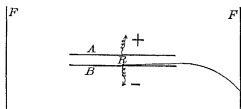


Fig. 93

from the radium will obviously only be able to escape from between the plates if the electric and magnetic forces upon them are exactly equal and opposite. Otherwise the particles will be deflected by whichever of the two fields is the stronger, and will strike one or other of the plates. The particles are projected at all angles to the magnetic field. Those which emerge from between the plates at an angle  $\theta$  with the magnetic field will have a velocity given by

$$Xe = H ev \sin \theta,$$

$$\therefore v = \frac{X}{H \sin \theta}$$

Thus for any given value of the angle  $\theta$  the rays which succeed in escaping from between the plates have a definite and calculable velocity.

On emerging from the plates the electrons are acted upon only by the magnetic field, and their deviation is pro-

portional to  $e/m$  where  $m$  is the mass corresponding to the velocity  $v$ . To measure the deviation the rays are allowed to fall upon a photographic film  $F, F$ , which is bent into a cylinder coaxial with the plates. The field is reversed during the experiment and the distance between the two traces on the film gives twice the magnetic deviation corresponding to that direction, from which  $e/m$  can be calculated. Hence  $v$  and  $e/m$  are known for each point on the film.

Bucherer found that the results so obtained agreed very closely indeed with the formula of Lorentz, but less closely with that of Abraham. The values of  $m_v/m_0$  given by the Lorentz formula are contained in Table VIII. It will be noticed that the increase in mass is inappreciable until  $v$  is at least one-tenth the velocity of light. The discrepancy between the Lorentz formula and the experimental results of Bucherer was less than one per cent.

TABLE VIII

$\beta$	$m_v/m_0$
01	1.000
10	1.005
30	1.048
50	1.115
60	1.250
70	1.400
80	1.667
90	2.294
95	3.203
98	5.025

113. **Passage of the  $\beta$ -rays through matter.** The absorption of the individual  $\beta$ -particles by matter would probably follow a law similar to that for the absorption of the  $\alpha$ -particles already considered, that is to say, all particles of the same velocity would come to rest after traversing a definite length of path in the matter. Unfortunately, owing to the much smaller energy of the particle, it is not yet possible to detect a single  $\beta$ -particle either electrically or by the fluorescent screen. We are thus limited to working with pencils containing large numbers of particles. We saw that the possi-

bility of finding the range of the  $\alpha$ -particles from experiments of this kind was due to the fact that the  $\alpha$ -particles are but little deflected by matter. With  $\beta$ -rays however, the deflections are very large. Thus absorption experiments corresponding to those of Bragg afford no information as to the range of the rays, since, owing to the numerous changes in the direction of the path in the matter, the actual path of the particles must be many times greater than the thickness of the absorbing material.

Experiments of this kind have been made by the author.<sup>(3)</sup> The  $\beta$ -rays were confined to a pencil of small angle by means of lead diaphragms, and the selected pencil of rays was rendered homogeneous (that is, of uniform velocity) by sorting out the complex beam emitted by radium into a "magnetic spectrum"

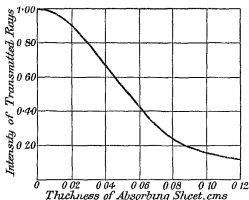


Fig. 94

by a transverse magnetic field. It was then allowed to fall normally upon absorbing screens of different materials and the proportion of the radiation transmitted was measured by an ionization method. The curve obtained for aluminum is shown in Fig. 94, the ordinates giving the ratio  $I_t/I_0$ , where  $I_t$  is the intensity transmitted through a thickness  $t$  of the substance, and  $I_0$  that of the incident radiation, for various thicknesses of absorbing material.

By measuring the velocity of the rays before and after passing through different thicknesses of an absorbing substance W. Wilson shewed that, like the  $\alpha$ -particles, the  $\beta$ -rays lose

velocity in passing through matter, but the rate of loss is very small. Owing to experimental difficulties the law of the loss of velocity could not be determined with any accuracy. In the case of the cathode rays however where the experiments are much easier it has been found that

$$V_0^4 - V^4 = kx \quad . \quad . \quad . \quad (102)$$

where  $V_0$  is the initial velocity,  $V$  the velocity after passing through a thickness  $x$  of the substance, and  $k$  a constant. This law possibly holds also for the  $\beta$ -particles. Owing to the intense scattering, however, it must be noted that the path of the particle in the absorbing screen is probably much greater than the thickness  $x$ .

If instead of forming the rays into a definite pencil they are allowed to fall at all angles on an absorbing screen, for example if the screen is placed directly above a layer of the radio-active substance, the absorption of the rays follows an exponential law, the intensity of the transmitted rays being given by the formula

$$I = I_0 e^{-\lambda x} \quad . \quad . \quad . \quad (103)$$

$\lambda$  being the coefficient of absorption of the rays. The coefficient increases as the velocity of the rays is reduced. Using absorbing screens of the different elements it has been shewn by the author that the value of  $\lambda/\rho$ , where  $\rho$  is the density of the substance, is a periodic function of the atomic weight of the absorbing substance.

**114. The scattering of the  $\beta$ -rays.** As has already been noted the  $\beta$ -particles are rapidly deflected from their original course during their passage through matter. The question was investigated by the author (3) using apparatus shewn in Fig. 95. The  $\beta$ -rays from radium at  $R$  were bent into the arc of a circle, of constant radius, defined by a series of stops, by a magnetic field at right angles to the plane of the paper. Since the radius of the path of the particles was fixed, for each value of the magnetic field rays of definite velocity given by  $\rho H = mv$ , where  $\rho$  is the radius of the circle and  $H$  the field, passed through the apparatus. The rays on emerging from the field fell normally upon an absorbing screen at  $P$ . The parallel beam was scattered

in the screen and rays emerged at all angles. When circular stops of known radius were placed at  $S$  the number of  $\beta$ -particles passing through  $S$  into the ionization chamber  $T$  was equal to the number which had not been deflected through an angle greater than the angle subtended at  $P$  by the radius of the stop.

The theory introduced by Rutherford to explain the scattering of the  $\alpha$ -particles (§ 107) should apply also to the  $\beta$ -particles with suitable changes in the constants. Here again it can be shewn that, at any rate for elements of fairly high atomic weight, the deflections produced by the electrons in the atom should be small

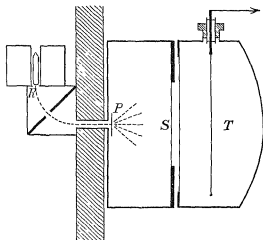


Fig. 95

compared with that due to the positively charged nucleus, while for thin sheets of the substance, the probability that the particle will meet with more than one measurable deflection is negligibly small. Since the charge on a  $\beta$ -particle is  $e$  the formula in § 107 becomes

$$\rho = \pi n t \frac{N^2 e^4}{4 T^2} \cot^2 \frac{\phi}{2},$$

where  $Ne$  is the charge on the nucleus. If  $\phi$  is small we may write  $\cot \frac{\phi}{2} = \frac{2}{\phi}$  and the equation then becomes

$$\rho = \frac{\pi n t N^2 e^4}{\phi^2 T^2}$$



This gives the fraction of the incident  $\beta$ -radiation deflected through an angle greater than  $\phi$ . Thus if the radius of the stop  $S$  subtends an angle  $\phi$  at the scattering foil  $P$  the intensity  $I$  of the radiation transmitted through the stop should be given by

$$\frac{I}{I_0} = 1 - \pi n l N^2 e^4 / \phi^2 T^2,$$

where  $I_0$  is the initial intensity of the radiation

Thus for  $\beta$ -rays of given velocity the curve shewing the relation between  $I/I_0$  and the thickness  $l$  of the scattering material should be linear for small thicknesses of the material. For stops of different angle the thickness required to cut down the radiation to the same extent, say to half value, should be directly proportional to the square of the angle of the stop. These results have been verified. It follows further that if  $l_m$  is the thickness required to cut down the radiation through a given stop to half value  $\frac{l}{l_m}$  should be directly proportional to  $N^2$ . Assuming that  $N$  is equal to the atomic number of the element, as proved by the experiments on the scattering of  $\alpha$ -rays,  $\frac{l}{l_m}$  should thus be directly proportional to the square of the atomic number of the scattering substance. The conditions are much more complex and the experiments more difficult for  $\beta$ -rays than for  $\alpha$ -particles, and the agreement between the theory and experiment is not very close. The discrepancy is not sufficient, however, to throw doubt upon a theory which is amply supported on other grounds.

**115. Nature and properties of the  $\gamma$ -rays.** The  $\gamma$ -rays are distinguished from the  $\alpha$ -rays and  $\beta$ -rays by their much greater penetrating power. The  $\gamma$ -rays from 30 milligrams of radium can easily be detected through 30 cm. of iron. They are not deviated by a magnetic field and, therefore, carry no charge. Their behaviour corresponds with the assumption that they are electromagnetic disturbances of extremely short wave length, even shorter than that of the most penetrating X-rays from a very hard bulb.

If in sufficient intensity they produce luminosity in a fluorescent screen, and affect a photographic plate. They also

produce ionization in gases, and are generally detected by this action

The relation of the  $\gamma$ -rays to the  $\beta$ -rays is the same as that of X-rays to cathode rays. In all probability the  $\gamma$ -ray is produced by the sudden emission of a  $\beta$ -particle from the radio-active atom or in some cases by the sudden stoppage of the  $\beta$ -particle within the material. Thus  $\gamma$ -rays are only produced by radio-active substances which are known to emit  $\beta$ -radiation. The actual connection is however somewhat obscure, as there seems to be no proportionality between the intensities of the two phenomena. Thus if the ratio of the  $\gamma$ -radiation to the  $\beta$ -radiation is taken as unity for radium C, then for thorium D it is about 0.74, for actinium D 0.077, and for uranium X as little as 0.02 or only one-fiftieth of that for radium C.

**116. Absorption of  $\gamma$ -rays** The absorption of a beam of  $\gamma$ -rays follows at any rate approximately an exponential law so that if  $I_d$  is the intensity after passing through a thickness of matter equal to  $d$

$$\frac{I_d}{I_0} = e^{-\mu d}. \quad . . . . (104)$$

The value of  $\mu$  depends upon the absorbing substance, and on the source of the rays. The rays from uranium are less penetrating than those from radium, their coefficient of absorption in lead being 0.725 as against 0.50 for the rays from radium. Taking the same source of radiation but different absorbing substances it is found that the value of  $\mu/\rho$  where  $\rho$  is the density is very nearly constant for the majority of the elements. It shows however a marked increase at both ends of the periodic table being exceptionally high both for the very light and the very heavy atoms.

**117 Characteristic  $\gamma$ -radiations** Rutherford<sup>(1)</sup> has recently shewn that the  $\gamma$ -rays from various radio-active substances contain homogeneous groups of rays. For example the rays from radium C contain a homogeneous group of rays which has a coefficient of absorption  $\lambda$  in aluminium of  $0.042\rho$  where  $\rho$  is the density of aluminium. Applying the fifth power law (§ 96) we find that this would be the coefficient of absorption in aluminium of

the characteristic  $K$  radiation of an element with an atomic weight 214. This is actually the atomic weight assigned to radium C. Hence the  $\gamma$ -radiation from radium C is apparently its characteristic X-radiation excited in it by the action of its own  $\beta$ -rays. Radio-actinium again gives out two sets of  $\gamma$ -rays having values of  $\lambda/\rho$  in aluminium of 9.2 and 0.070. These are found to agree respectively with the absorption coefficients (as calculated by the fifth power law) of the  $K$  and  $L$  radiations for an element of atomic weight 228, which is that provisionally assigned to this element. Other homogeneous  $\gamma$ -radiations have been discovered, such as that from thorium D which gives a value of  $\lambda/\rho$  of 0.035, and which is the most penetrating radiation known, and a very penetrating series of radiations from radium C. These apparently belong to a  $J$  series of characteristic rays which have not yet been definitely isolated in the X-ray part of the spectrum, though evidence of their existence is gradually accumulating.

It may further be noted that the less penetrating  $\gamma$ -rays such as those from actinium or radium E will excite the characteristic X-radiation of elements having atomic weights ranging from silver to didymium. The  $\gamma$ -rays are thus merely X-rays of very short wave length corresponding to the characteristic X-radiations of the elements of high atomic weight.

**118. Determination of the wave length of  $\gamma$ -rays.** The matter has been placed beyond all doubt by the determination which Rutherford made of the wave length of the  $\gamma$ -rays. The method adopted was an interesting modification of that of the X-ray spectrometer already described. As the glancing angle decreases with the wave length it is very small for  $\gamma$ -rays, only about 1 or 2 degrees, and hence could not be measured with any precision. To overcome the difficulty a crystal  $S$  of rock salt was mounted with cleavage planes parallel to the line  $RO$  (Fig. 96), the source of  $\gamma$ -radiation being placed at  $R$  and a photographic plate at  $O$ . The  $\gamma$ -rays strike the crystal at all angles but only those which fall upon it in such a way that the angle between them and the reflecting planes is the glancing angle for the particular wave length will

be reflected. The rays are thus left as it were to pick out their own reflecting planes, and beams of reflected rays  $AB$  and  $A'B'$  will emerge from the crystal and fall on the photographic plate.

Neglecting the absorption of the crystal, which will be very small, the energy in the primary beam must be equal to the energy transmitted plus the energy reflected. Hence a ray such as  $RA$  which is selectively reflected will suffer a much greater loss of energy in going through the crystal than rays which pass through without any loss by reflection. Thus in the direction  $RA$  produced the rays will be relatively enfeebled and thus the effect on the photographic plate will be small. The reflecting plane thus casts a shadow on the photographic plate at a point  $C$  in the direction  $RA$  produced. Similarly

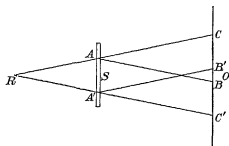


Fig. 96

the plane  $A'$  casts its shadow at  $C'$ . It is evident that the angle  $CAB$  subtended by the distance between corresponding bright and dark lines at the crystal is equal to twice the glancing angle for the rays. In this way by measuring the distance  $CB$  on the plate and the distance of the plate from the crystal the angle of selective reflection for the rays used can be accurately determined.

The values of the glancing angle for the  $\gamma$ -rays from the mixture of radium B and radium C used for the experiment ranged from  $41''$  to  $4^\circ$ . The corresponding wave lengths ranged from  $0.71 \times 10^{-9}$  to  $4 \times 10^{-9}$  cm. The most penetrating rays thus measured had about one-eighth of the wave length of the characteristic  $K$  radiation of silver. Rays of still greater penetration, and hence of still shorter wave length, are known to exist, but their glancing angles are too small to be measured.

**119 Secondary  $\gamma$ -rays** In the same way that a primary beam of X-rays gives rise to scattered X-radiation so a beam of  $\gamma$ -rays gives scattered  $\gamma$ -radiation when it falls on a radiator. The distribution of the secondary radiation round the radiator is very similar to that of the scattered X-rays.

In addition to the scattered  $\gamma$ -radiation, secondary  $\beta$ -rays are liberated when the  $\gamma$ -rays fall on a radiator. This radiation is very much more intense in the direction in which the rays are travelling than in the reverse direction, the eccentricity being generally much more pronounced than in the case of X-rays. The ratio for aluminium is as high as 6:1. This result might have been expected from equation (93), since  $u/v$  the ratio of the forward to the transverse velocity is proportional to the velocity of the electron ejected, which is in this case a swift moving  $\beta$ -ray having a velocity which may be more than ten times that of the cathode particles ejected by X-rays.

**120. Production of  $\gamma$ -rays from  $\beta$ -rays** The reverse effect, that of the direct production of  $\gamma$ -rays by  $\beta$ -rays, has also been demonstrated. The number of  $\beta$ -particles emitted even by a powerfully radio-active substance is quite insignificant in comparison with the number of electrons in the cathode rays of an ordinary X-ray tube. As only a very small fraction of the energy of the  $\beta$ -rays is transformed into  $\gamma$ -radiation, the effect has been somewhat difficult to demonstrate. The method used is indicated in Fig. 97. The measuring apparatus was a simple gold leaf electroscope, *E*. For measurements on the  $\gamma$ -rays an electroscope of this type is generally preferred to the use of an electrometer with a separate ionization chamber. Owing to the great penetrating power of the radiation it would be quite impossible to shield the connecting

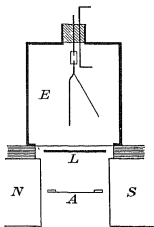


Fig 97

tubes and the electrometer from the action of the rays, and thus loss of insulation would result owing to the radiation ionizing the gas in the electrometer and tubes. This would cause a distinct and not readily calculable loss of charge.

The electroscope is usually constructed of lead walls 2 mm in thickness, so as to cut off all secondary  $\beta$ -radiation from the surrounding air, table, walls, etc. This thickness causes little appreciable diminution in the intensity of the  $\gamma$ -rays themselves.

A source of  $\beta$ -rays (radium B) was chosen which while rich in  $\beta$ -rays was yet poor in  $\gamma$ -radiation. This was spread on a thin sheet of paper at *A*, the paper being used to reduce as much as possible the  $\gamma$ -radiation which might be excited by the  $\beta$ -rays falling upon the support. The substance was placed between the poles *N*, *S* of an electromagnet. The lower face of the electroscope was closed by a thin sheet of aluminum leaf. When the  $\beta$ -rays were deflected away from the electroscope the current was due solely to the  $\gamma$ -rays from the radium B, and was therefore quite small.

If, however, a lead plate sufficiently thick to absorb all the  $\beta$ -rays was placed at *L*, immediately below the electroscope, and the field removed so that the  $\beta$ -rays fell upon *L*, the ionization in *E* at once increased. This could not be due to the  $\beta$ -rays themselves, as they were unable to penetrate the lead. If, however, the field was again applied so as to prevent the  $\beta$ -rays from reaching *L* the effect at once ceased. The increased ionization must therefore be due to  $\gamma$ -radiation set up in *L* by the impact of the  $\beta$ -rays upon it.

The matter was further investigated by Rutherford and his pupils. The  $\gamma$ -rays produced by the impact of the  $\beta$ -rays from a radium compound on a lead radiator were allowed to fall on a second lead block, and the velocity of the secondary  $\beta$ -rays produced by them from the block was measured. It was found that just as in the case of the secondary cathode rays produced by the impact of X-rays on a radiator, the velocity of the secondary  $\beta$ -rays produced by the action of the  $\gamma$ -rays on the metal was the same (to an accuracy of one or two per cent) as that of the  $\beta$ -rays used in exciting the  $\gamma$ -radiation.

The most illuminating experiments on the subject are, how-

ever, those recently made by Ellis(5) These experiments practically repeat with  $\gamma$ -rays the experiments of de Broglie, Robinson, and others with X-rays, and the apparatus employed was practically identical with that used by Robinson and described on p 197 A narrow tube containing radium emanation served as a source of  $\gamma$ -rays, and the radiator to be investigated was wrapped immediately around the tube This combination took the place of the radiator  $R$  (Fig 80) and was placed in the same position The thickness of material used, about 3 mm., was more than sufficient to stop the  $\beta$ -radiation from the source itself The  $\beta$ -rays emerging were therefore all secondary  $\beta$ -rays produced within the radiator by the action of the incident  $\gamma$ -radiation. Knowing the magnetic field employed, which was of course much higher in these experiments than in those with X-rays, the velocity of any group of  $\beta$ -rays could be determined from their position on the photographic plate The energy of the rays could be calculated from their velocity, the necessary correction being made for the variation of mass with velocity

For each of the substances employed as radiators the  $\beta$ -ray spectrum obtained shewed three main lines The exact position of these lines varied however with the atomic number of the radiator, the energy being greater as the atomic number was less Following the analogy of the X-ray transformations we may account for these phenomena by assuming that the lines are due to the ejection from the  $K$  level of the radiator of electrons by three distinct homogeneous  $\gamma$ -radiations Let  $\nu$  be the frequency of one of these radiations, and  $W_N$  the energy associated with the  $K$  level of an element of atomic number  $N$  Then the energy  $E_N$  of the ejected  $\beta$ -particle should be  $h\nu - W_N$  As  $W_N$  decreases with  $N$ , the energy of the particles should increase as the atomic number of the radiator decreases The theory can be tested numerically since the energies of the  $K$  levels are known from X-ray determinations, and  $E_N$  is measured For a given  $\gamma$ -radiation  $E_N + W_N$  should be constant This is found to be the case, as is shewn in Table IX (p 240) The energies, as is customary in these measurements, are expressed in "volts" (See § 98.)

The homogeneous groups of secondary  $\beta$ -rays emitted by a radiator under the influence of  $\gamma$ -radiation are thus due to the transformation of the  $\gamma$ -rays in the various atomic levels in accordance with the ordinary quantum relations. When the particular level in which the transformation takes place has been identified the results can obviously be employed to determine the wave length of the incident  $\gamma$ -radiation, and provide the most practicable method of determining wave lengths in this part of the spectrum.

TABLE IX

	Ba	W	Pt	Pb	U	
$E_N$	2.53	2.20	2.12	2.03	1.74	$> 10^5$ volts
$W_N$	.37	.69	.78	.89	1.18	"
$E_N + W_N$	2.90	2.89	2.90	2.92	2.92	"

121 **Characteristic  $\beta$ -rays.** It has been known for some considerable time that the  $\beta$ -rays from a radio-active substance contain groups of rays of definite velocity, characteristic of the substance, superimposed on a background of "general" radia-

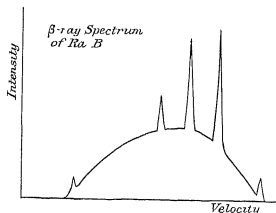


Fig. 98

tion. The  $\beta$ -ray spectrum of radium B, for example, shews five prominent lines, as indicated in Fig. 98(c). The results described in the previous section suggest that these may be due to a transformation of the characteristic  $\gamma$ -rays of the substance in its own material.



This hypothesis has been confirmed by Rutherford by an ingenious method. It is known that radium B and lead are isotopic. Their absorption levels should, therefore, be identical and the secondary  $\beta$ -rays emitted by the two under stimulus of the same frequency should be identical. On measuring the secondary  $\beta$ -ray spectrum from lead exposed to the  $\gamma$ -rays from radium B it was found to be identical with the natural spectrum of radium B, in full agreement with the hypothesis.

The origin of the "general" or continuous  $\beta$ -ray spectrum of a radio-active substance is not so clear. The evidence seems to indicate that these particles are emitted from the nucleus of the radio-active atom, a single  $\beta$ -particle being ejected from each disintegrating atom. It is not, however, obvious why the velocities of these particles should vary over so wide a range.

**122 Origin of characteristic  $\gamma$ -radiation** The accurate measurement of the wave lengths of the characteristic  $\gamma$ -rays by the method detailed in § 120 has rendered it possible to make speculations as to their origin. We have seen that the characteristic X-ray spectra are adequately explained by the hypothesis that each line is emitted by an electron which falls spontaneously from a level of greater to one of lower potential energy. The existence of such levels in the X-ray part of the spectrum is confirmed by absorption experiments (§ 95). In the case of  $\gamma$ -rays these absorption experiments are not available, and we must rely on the evidence of the emission spectra alone.

The "levels" concerned must, on account of the very high frequency of the corresponding radiations, lie within the  $K$  level, and the fact that the inverse square law of force holds within the  $K$  ring practically up to the nucleus itself shews that there are no electrons in this region. The levels, if they exist at all, are, therefore, levels in the nucleus itself. Assuming that the quantum laws are applicable within the nucleus of the atom, we must have

$$h\nu = W_B - W_A,$$

where  $\nu$  is the frequency of the  $\gamma$ -radiation emitted by the passage of an electron from a level of energy  $W_B$  to one of energy  $W_A$ .

It is of course always possible, by taking a sufficient number of levels, to satisfy the relation. The validity of the method will depend on its being able to account for a large number of homogeneous rays with a comparatively small number of levels. Since any transference of an electron from a higher to a lower level should give rise to a line in the spectrum, the number of lines emitted should be equal to the number of possible combinations between the levels assumed. Thus four levels,  $A$ ,  $B$ ,  $C$ , and  $D$ , should give rise to spectrum lines corresponding to the transformations  $D - A$ ,  $C - A$ ,  $B - A$ ,  $D - B$ ,  $C - B$ , and  $D - C$ , or six in all. Ellis(8), to whom both the measurements and their interpretation are due, has found it possible to interpret the  $\gamma$ -ray spectrum of radium B by assuming the existence of seven different energy levels in the nucleus, with a maximum discrepancy between the calculated and the observed frequencies of the spectrum lines of less than 1 per cent. Of the 21 lines to which these levels should give rise, 14 have already been identified. The evidence is thus strongly in favour of the suggestion put forward by Ellis, and of the applicability of the quantum theory within the nucleus.

In addition to its characteristic line spectrum the radioactive substance also emits a continuous  $\gamma$ -ray spectrum. This continuous  $\gamma$ -radiation is probably concerned with the emission of the continuous  $\beta$ -ray spectrum.

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- (7) ELLIS *Proc. Roy. Soc. A*, 101, p. 1, 1922.
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## CHAPTER XIII

### RADIO-ACTIVE CHANGES

123. **Disintegration of uranium.** We have already considered the nature of the radiations emitted by radio-active substances. We must now investigate more closely the nature of radio-activity itself. Uranium supplies us with perhaps the simplest case. Uranium and its salts were found to give off both  $\alpha$ - and  $\beta$ -rays,  $\gamma$ -rays of small intensity attending the latter. Using a thick layer of the substance practically the whole of the effect on a photographic plate is due to the  $\beta$ -radiation, since owing to the great absorbability of the  $\alpha$ -rays only those from a comparatively thin layer can reach the surface and at the best of times the photographic effect of an  $\alpha$ -ray is small. In 1900 Sir Wm. Crookes shewed that it was possible by a single chemical operation to obtain uranium which was photographically inactive, while the whole of the photographic activity was concentrated in a very small residue, free from uranium and consisting chemically of the small traces of the impurities present in the original salt. This residue to which he gave the name of uranium X could be obtained many hundred times as active weight for weight as uranium itself, while the major fraction which could be shewn by chemical tests to be uranium was photographically inactive. The method originally used was to precipitate the uranium with ammonium carbonate and to dissolve the precipitate in excess of the reagent. On filtering a trace of precipitate remained behind on the filter paper. This contained the uranium X. The same separation can also be carried out by other methods. So far the phenomena resemble very closely the separation of two ordinary chemical substances by the usual methods of analysis. However, if the two fractions are laid aside for two or three months it is found that the uranium has recovered the whole

of its original activity while that of the uranium X has completely disappeared. The loss of activity of the uranium was therefore only temporary in character, while the increased activity of the separated uranium X was equally short lived.

It was further found that the total activity, as measured by the photographic effect, that is, by the  $\beta$ -rays, was constant at any time before or after the separation, the gain of activity of the uranium exactly corresponding to the loss of activity of the uranium X. The measurements are most conveniently made by the electrical method. The substance to be examined is spread in a thin layer over the lower plate B of the parallel

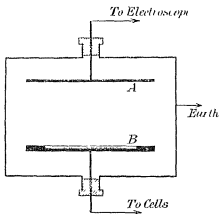


Fig. 99

plate ionization chamber (Fig. 99) which is used as the high potential plate and connected to a battery of cells. The upper plate A is connected to the electroscope or electrometer, and the saturation current is measured in the usual way. The saturation current is taken as proportional to the activity of the substance. In order to be comparable with the photographic effect which we have been describing and which as has been pointed out is due to the  $\beta$ -rays, the substance must be covered with 1/10 mm. of aluminum to cut off all the  $\alpha$ -radiation.

Using two chambers of this type we can investigate more closely the change of activity with time in the two fractions. The results for uranium are shown in Fig. 100. The two

curves are complementary, the sum of the two ordinates at any point being the same.

By plotting the *logarithms* of the currents against the time it is found that the decay curve of the uranium X follows an exponential law, that is, if  $I_t$  is the activity at a time  $t$ , then

$$\frac{I_t}{I_0} = e^{-\lambda t} \quad . \quad . \quad . \quad (105)$$

where  $I_0$  is the activity at the moment when the measurements began, and  $\lambda$  is a constant, which is known as the *radio-active constant* for the particular substance, in this case uranium X.

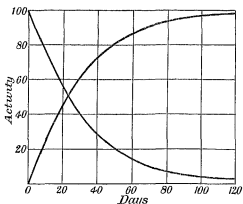


Fig 100

Since the curves are complementary the recovery curve for the uranium can be expressed in the form

$$\frac{I_t}{I_0} = 1 - e^{-\lambda t} \quad . \quad . \quad (106)$$

where  $t$  is the time which has elapsed since the uranium was completely freed from uranium X, and  $\lambda$  is the same constant as before

Differentiating the expression for the decay of uranium X we have

$$\frac{dI}{dt} = -\lambda I_0 e^{-\lambda t}.$$

But  $I_0 e^{-\lambda t}$  is the quantity of the uranium X still present =  $I$  say. Thus

$$\frac{dI}{dt} = -\lambda I \quad . \quad . \quad . \quad (107)$$

In other words *the rate of decay at any moment is simply proportional to the quantity of radio-active matter still present*, a very important result.

The uranium which has been freed from  $\text{Ur X}$  is inactive as measured by its  $\beta$ -ray effect. If, however, we remove the aluminium screens from the two fractions in Fig 99 we find that the ionization is now nearly all due to the uranium itself, the activity of the separated fraction being negligible in comparison with that of uranium itself. In other words uranium itself gives out  $\alpha$ -rays but no  $\beta$ -rays while the uranium  $\text{X}$  gives out  $\beta$ -rays but no  $\alpha$ -rays.

The rate of decay of activity of the  $\text{Ur X}$  has been shewn by many experiments to be quite independent of external conditions. It is the same whether the two fractions are kept separate or whether they are enclosed in the same tube, the same whether the product is exposed to the air or sealed in a thick walled lead box, so as to be freed as far as possible from all external influences. It is quite independent of temperature being the same at the temperature of liquid air as at a red heat. It does not depend on the processes used for the separation of the two substances and is therefore presumably independent of the state of combination of the substance. The growth of activity of the uranium salt is the same if it is changed into some other salt of the metal, or whether it is solid or in solution. It is in fact a constant of the substance itself.

**124. Theory of radio-active change.** It is at first sight somewhat remarkable that the processes of recovery and decay should be so closely connected even when the two fractions are separated from each other in such a way as to preclude all possibility of interaction between them. The effects however have found a complete explanation on the following assumptions

(1) That there is a constant production of the new radio-active substance ( $\text{Ur X}$ ) by the radio-active body (uranium)

(2) That the new substance ( $\text{Ur X}$ ) itself disintegrates according to an exponential law, with a constant equal to the radio-active constant  $\lambda$  for the change

Suppose that from the given mass of uranium  $q_0$  particles of uranium X are produced per second. The activity of the particles produced in a short interval of time  $dt$  will at their moment of production be equal to  $Kq_0 dt$ , where  $K$  is a constant measuring the effect produced on our electroscope by one particle of Ur X. The activity of these particles after a time  $\tau$  will be given by

$$Kq_0 e^{-\lambda \tau} = dI \quad . \quad (108)$$

Suppose we wish to know the total activity of the uranium at a time  $T$  after it has been completely freed from the product Ur X. Then the time which has elapsed since the formation of the particular particles we are dealing with is equal to  $T - t$  where  $t$  represents its moment of formation. The effect due to these particles is thus  $Kq_0 e^{-\lambda(T-t)}$  and the total activity at the time  $T$  is therefore given by

$$\begin{aligned} I_T &= \int_0^T Kq_0 e^{-\lambda(T-t)} dt \\ &= \frac{Kq_0}{\lambda} (1 - e^{-\lambda T}) \quad . \quad (109) \end{aligned}$$

The maximum activity is reached when the process has been going on for a sufficient time to make  $e^{-\lambda T}$  negligible, and is given by

$$I_0 = \frac{Kq_0}{\lambda}$$

Calling this value  $I_0$  we have

$$\frac{I_T}{I_0} = 1 - e^{-\lambda T}$$

which agrees with the experimental results. It will be noted that  $\lambda$  is the constant measuring the rate of decay of the product.

The equilibrium state is obviously reached when the loss of activity due to decay of the product is equal to the rate of formation of the product from the original substance. Since the product is always decaying according to the exponential law, whether it is mixed with the parent substance or separated from it, it follows that uranium is constantly producing a new substance uranium X from itself at a definite constant rate. When equilibrium has been established it is evident that the

quantities of the two substances present will bear a constant ratio to each other.

The possibility of separating uranium X from uranium in various chemical ways shews that the two substances are chemically distinct. This is still more obvious in the case of radium, in which, as we shall see, the first product of the radio-active change is a gas. Moreover, the uranium not only gives uranium X but in the process emits  $\alpha$ -particles which, as we have already seen, are material in nature, being neither more nor less than charged atoms of helium. It is impossible in view of these and many other facts which will appear throughout the discussion to avoid the conclusion that the atom of uranium disintegrates spontaneously, giving off a charged helium atom and forming a new element uranium X which, although owing to its rapid decay it is always present in quantities too small to admit of direct chemical investigation, can be detected by the  $\beta$ -radiations which it emits. The product of the decay of uranium X has been identified as a new radio-active substance, Ionium, which in its turn is proved to be the origin of the element radium. Owing to the relation between the radio-active constants of the various products the investigation of this sequence has proved difficult. We will therefore postpone its consideration until we have considered the case of radium itself in which owing to its intense activity, and to special circumstances which render the separation of the various products easy, the phenomena of successive changes are easier to follow.

**125 Theory of successive transformations** The case we have so far considered has been a very simple one for two reasons. In the first case the amount of uranium breaking up during the time of our experiments is so infinitesimally small that we can without error regard the amount of uranium present during the experiment as constant. In the second place the substance formed by the disintegration of the uranium X is so feebly radio-active that its effect upon the electroscope is inappreciable. In general these simple conditions do not hold. Radium, for example, which has been prepared for more than a few days



is found to contain at least five radio-active substances whose activity must be taken into account. The same principles which were successful in explaining the decay and recovery curves of uranium and its product can also be applied to the more complex cases with equal success. For convenience these principles have been stated in the form of six propositions by Sir Ernest Rutherford, to whom the theory is due.

(1) The activity shewn by radio-active substances is due to the disintegration of the atom.

(2) A definite fraction of the total number of atoms present become unstable in a given small interval of time.

(3) In most cases this instability and disintegration is accompanied by the emission of energy in the form of  $\alpha$ -,  $\beta$ - and  $\gamma$ -rays, by  $\alpha$ -rays alone or by  $\beta$ - and  $\gamma$ -rays alone. Occasionally it takes place without emission of ionizing radiations. If radiations are emitted it is assumed that the fraction of the atoms changed per second can be measured by the intensities of the radiations emitted.

(4) The expulsion of a single  $\alpha$ -ray of atomic weight 4 gives rise to an atom differing in atomic weight by four units from the parent atom. The expulsion of  $\beta$ -particles, which have a mass insignificant compared with that of a hydrogen atom, produces no change in atomic weight, but only in the internal structure of the atom.

(5) At any time after disintegration has commenced there exist together in the substance

(a) the unchanged substance,

(b) the immediate product of its disintegration of the same or smaller atomic weight,

(c) any product or products formed from the disintegration of (b) if it is itself radio-active.

(6) Each of the products of radio-active change is a new element, and has different chemical properties from those of the parent atom. This is shewn by their different behaviour to various chemical reagents as in the case of uranium. It is still more clear in the case of radium in which the first decomposition product is a gas.

The general problem may be stated as follows: Suppose we

have a series of elements  $A, B, C, D,$  such that  $A$  changes into  $B, B$  into  $C, C$  into  $D,$  and so on. Given that the number of atoms of each present at a given moment in a substance is  $a, b, c, d, \dots$  respectively to find the number of each still present in the mixture after a time  $t$  has elapsed. The general problem is capable of solution, but it will be simpler and more instructive to confine our attention to one or two illustrative cases which are met with in actual practice.

By assumption (2) we have for each of the substances

$$dn/dt \propto n,$$

where  $n$  is the number of atoms of that substance actually present at the given moment. Thus

$$\frac{dn}{dt} = -\lambda n, \quad n = n_0 e^{-\lambda t}, \quad (110)$$

that is to say, each element by itself decays according to an exponential law.  $\lambda$  is known as the radio-active constant for the substance.

We shall see later that the decomposition of the atoms follows a probability law, and that  $\lambda n$  is only the most probable value of the number disintegrating per second. When, however, as is usually the case, the total number of atoms is large, the actual value over a finite interval of time will not differ from its most probable value by an appreciable amount.

It must be noted that  $\lambda n$  is also the rate of formation of the new substance  $B$ . We have already seen that  $\lambda$  is independent of the most extreme changes in external and chemical conditions. It is also independent of the age of the substance. Experiments have been made with radium emanation which loses half its activity in 3.85 days, over a period exceeding three months. The rate of decay throughout was strictly exponential, the constant  $\lambda$  being the same at the end of the experiment as at the beginning. It is thus the same for emanation which is freshly formed as for emanation three months old. In fact the break up of the atom depends solely on the law of probability and the nature of the atom.

Two other ways of defining the rate of decay of the radio-

active substance are often used. The *half period value* is the time taken for the activity of the substance to fall to one-half its original value. This can be obtained from (110) by putting  $n/n_0 = \frac{1}{2}$  and solving for  $t$ . Thus  $-\lambda t = \log_e \frac{1}{2}$ ,

$$t = \frac{\log_e 2}{\lambda} = \frac{0.693}{\lambda} \quad (111)$$

The *average life* of the radio-active atom can also be calculated. The number of atoms changing during a short interval  $dt$  at a time  $t$  since the separation of the substance  $= \lambda n dt$ . Also  $n = n_0 e^{-\lambda t}$  and thus  $dn = -\lambda n_0 e^{-\lambda t} dt$ . These atoms have had a life of  $t$  seconds. The average life of all the atoms of the substance is therefore

$$\begin{aligned} \frac{1}{n_0} \int_0^\infty t \lambda n_0 e^{-\lambda t} dt \\ = \frac{1}{\lambda} \end{aligned} \quad (112)$$

**126. Radio-active equilibrium.** Suppose we commence with some substance such as uranium or radium the life of which is comparatively long compared with the time occupied by our experiments. The average life of uranium, for example, is about  $7 \times 10^9$  years and that of radium about 2880 years. Over any ordinary period of time therefore the quantity of the original radio-active substance which we will call  $A$  remains constant, and hence fresh radio-active matter is produced from it at an approximately constant rate, which will be equal to  $\lambda_1 a_0$  where  $a_0$  is the number of atoms of  $A$  present, and  $\lambda_1$  its radio-active constant. If  $B$  is the immediate disintegration product of  $A$ ,  $B$  is being formed in the substance at this constant rate  $\lambda_1 a_0$ . But the rate at which  $B$  disintegrates is proportional to the amount of  $B$  actually present, and thus increases with the increase in the quantity of  $B$ . Hence a point will come when the rate of disintegration of  $B$  is equal to its rate of formation from  $A$  and the amount of  $B$  in the substance will then remain constant. The rate at which  $B$  increases is equal to the difference between its rate of formation from  $A$  and its rate of disintegration into  $C$ . Thus

$$db = \lambda_1 a_0 dt - \lambda_2 b dt \quad (113)$$

where  $b$  is the number of atoms of  $B$  present at the given instant. Similarly for the element  $C$  we have

$$dc = \lambda_2 b dt - \lambda_3 c dt$$

It is evident that the amounts of  $B$ ,  $C$ , . . . present in the mixture will become constant when

$$\lambda_1 a_0 = \lambda_2 b = \lambda_3 c = \dots \quad (114)$$

Thus when radio-active equilibrium, as it is called, has been established the various radio-products will bear to each other a constant ratio which is inversely proportional to their radio-active constants. Conversely, if on analysis two radio-active substances are always found occurring in nature in the same ratio, one of them must be a product, direct or indirect, of the other. Thus the fact that the proportion of radium to uranium in minerals is always constant is evidence that radium is a product of the disintegration of uranium.

A hydrostatic analogy may prove useful in understanding the process. Suppose we have a series of tanks  $P$ ,  $Q$ ,  $R$ , . . . emptying one into the other as shewn in Fig. 101. The rate at which water flows out of any tank will be proportional to the area of the aperture and to the height of the water in the tank at the moment under consideration. In other words, supposing the tanks to have the same area of cross section, the flow will be proportional to the quantity of water in the tank. The rate of efflux of the water thus follows the same law as the rate of decomposition of a radio-active substance.

Supposing now that the water in the tank  $P$  is kept at a constant level. This will correspond to the case we have just been considering. Water will rise in each tank until the rate of efflux, which is proportional to the quantity of water in the tank, is equal to the rate at which water pours into it from the tank above. When equilibrium is established the rate of flow will be constant throughout, and the height of the water in the



Fig. 101

different tanks will be inversely proportional to the size of their apertures. If the aperture is small the height of the water will be large, if on the other hand it is large a comparatively small height of water will produce the necessary efflux. Similarly when equilibrium is established substances of quick decay, for which the radio-active constant is large, will be present in relatively small proportions while those which decay slowly and for which the radio-active constant is small, will be present in large amounts. It is thus only the comparatively long-lived radio-active substances, such for example as radium itself, which we could expect to obtain in measurable quantities.

The case which we have just considered constitutes what may be described as permanent radio-active equilibrium the amounts of each substance present remaining constant after equilibrium has once been reached. Let us suppose now that water is no longer poured into the first tank  $P$ , but that  $P$  has a small aperture so that the rate of efflux is small. This will correspond to the case of the decomposition of a radio-active substance of small but appreciable radio-active constant. The rate of flow of water through the system will obviously be governed by that of the tank with the smallest aperture, in this case by  $P$ . It is evident, therefore, that when equilibrium has been established the quantity of water in each tank will be proportional to the quantity remaining in  $P$ , since the rate of flow through the system is governed by this factor. A little consideration will shew that the relative amounts of water in the different tanks will be very nearly the same as if the level in  $P$  were maintained at the value which it has at the moment of observation by a continuous influx of water. It will actually be slightly larger. The two cases will approximate more nearly to each other the slower the rate of efflux from  $P$ .

We thus get a state which we may describe as that of *transient equilibrium*, the relative quantities of water in each tank remaining constant, but each of the quantities decreasing in absolute magnitude proportionately to the quantity in the first tank.

This case corresponds to that of a radio-active substance which gives rise by its disintegration to a series of radio-active

substances, the average life of which is short compared to its own. For example, radium emanation which has an average life of 5.55 days gives rise to successive radio-active substances which have average lives of 4.32 minutes, 38.7 minutes, and 28.1 minutes respectively. Thus, if radium emanation is placed in an enclosed space and left to decay, after equilibrium has been established, which takes place in about four or five hours, the quantity of any one of the products present is simply proportional to the quantity of the emanation remaining in the vessel. This is a case of transient radio-active equilibrium. It can be shewn that in this case the quantity of each product actually present is about one per cent greater than the value which it would finally attain if the quantity of emanation present were maintained at its actual value at that instant by an external source.

The problems arising can easily be solved if required by an application of the principles enunciated by Rutherford.

Taking the case we have just considered for an example, suppose that  $A, B, C, \dots$  are a series of such elements so that  $A$  changes into  $B$ ,  $B$  into  $C$ , and so on. Then if the substance at the beginning consists only of the element  $A$  (for example only of radium emanation), and if  $a, b, c, \dots$  are the number of atoms of each element present at a time  $t$  from the start, and  $\lambda_a, \lambda_b, \lambda_c, \dots$  are the corresponding radio-active constants, we have

$$a = a_0 e^{-\lambda_a t}$$

where  $a_0$  is the number of atoms of  $A$  with which we commenced the experiment. Also by (113) we have

$$db = \lambda_a a dt - \lambda_b b dt,$$

$$dc = \lambda_b b dt - \lambda_c c dt,$$

and so on. Substituting for  $a$ , we have

$$\frac{db}{dt} = \lambda_a a_0 e^{-\lambda_a t} - \lambda_b b$$

The solution of this equation is of the form

$$b = a_0 (k_1 e^{-\lambda_a t} + k_2 e^{-\lambda_b t}). \quad (115)$$

Now  $b = 0$  when  $t = \infty$ , since all the substances eventually disintegrate completely;  $\therefore k_1 = -k_2$ . Differentiating the equa-

tion and applying the conditions that when  $t = 0$ ,  $\alpha = \alpha_0$  and  $b = 0$ , we find  $k_1 = \frac{\lambda_a}{\lambda_b - \lambda_a}$ , and thus finally

$$b = \frac{\alpha_0 \lambda_a}{\lambda_b - \lambda_a} (\epsilon^{-\lambda_a t} - \epsilon^{-\lambda_b t}) \quad (116)$$

The method can obviously be continued to give the corresponding value of  $c$ , and so on. If  $\lambda_b$  is large compared with  $\lambda_a$ , then when  $t$  is comparatively large  $\epsilon^{-\lambda_b t}$  will be small compared with  $\epsilon^{-\lambda_a t}$  and the quantity of  $b$  present will thus be proportional to  $\alpha_0 \epsilon^{-\lambda_a t}$ , that is, to the quantity of  $A$  remaining; the result we have already obtained from general considerations.

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## CHAPTER XIV

### RADIUM AND ITS PRODUCTS

127. The nature and properties of radium. The principles we have been considering will be made clearer, and the evidence for them more conspicuous, if we study in detail one series of radio-active changes. That of radium is the most suitable for the purpose, not merely on account of its intrinsic importance but also owing to various accidental causes which render the phenomena particularly clear.

Radium can be isolated from uranium ores, in which it exists as a product of the radio-active disintegration of the uranium. It is obtained by the processes used in the extraction of barium from the ores, to which element it bears a close chemical resemblance. It can be obtained free from barium by repeated fractional crystallization of the bromide, the radium salt being somewhat less soluble in water than the corresponding salt of barium, with which, however, it is isomorphic.

The proof of the elementary nature of radium is now complete. It is afforded in the first place by the spectrum, which is characteristic of the metal, and differs from those of all other elements. The lines in the radium spectrum have now been analysed into their component series, and are found to present the common characteristics of the metals of the alkali earths. Applying the usual laws of spectra the spectrum of radium is found to correspond to that of an alkali earth metal of atomic weight about 225.

Radium has now been obtained in sufficient quantities and of sufficient purity to enable its atomic weight to be obtained by direct chemical methods. The method employed is that of precipitating the radium chloride with silver nitrate, and weighing the silver chloride formed. By repeated crystallization Madame Curie obtained a product so pure that the strongest



barium line was only feebly visible in the spectrum of the salt. In this way the atomic weight was found to be 226.4. Other recent determinations give values ranging from 225.95 to 226.15. The atomic weight of radium may thus be regarded as known within these narrow limits.

The value of the atomic weight of radium is strong evidence for the disintegration theory of its formation. It is known that the conversion of uranium into radium is attended with the expulsion of three  $\alpha$ -particles, each of which has an atomic weight of 3.99. Thus on the disintegration theory the atomic weight of radium should be less than that of uranium by the weight of three  $\alpha$ -particles or atoms of helium. The atomic weight of uranium is 238.5. That of radium should therefore be  $238.5 - 3 \times 3.99$ , or 226.5, in satisfactory agreement with the chemical determinations.

Radium can be obtained in metallic form. It is a silver white metal, melting at about  $700^{\circ}\text{C}$ , and beginning to volatilize at a slightly higher temperature. It is attacked by air forming a nitride, and by water forming the hydroxide. It forms a series of salts similar in properties and appearance to those of barium. It thus possesses in every particular the characters of a metallic element of the alkali earth group.

**128 Radium emanation.** The first product of the disintegration of radium is the heavy inert radio-active gas known as radium emanation. It is found that a sample of pure radium emits this gas at a constant, definite rate, the emission being attended by the expulsion of an  $\alpha$ -particle. The phenomena of radio-active change are peculiarly striking in this instance, the parent substance being a metallic solid, while the disintegration product is an inert gas which can thus be easily separated from it by purely physical means.

The existence of a radio-active gas was first recognized in the case of thorium. It was noticed that the measurements of the activity of this substance were liable to peculiar fluctuations, being for example much diminished in a strong draught of air. The phenomena were finally traced by Rutherford to the emission by the thorium of a substance which was carried

about by the air currents, and thus gave rise to the observed peculiarities. In order not to prejudice future investigation these products were called "emanations," a name which has stuck to them in spite of subsequent research. They are now known to possess all the properties of ordinary gases of high atomic weight.

Investigation of radium salts immediately showed that a similar emanation was given off by radium. Owing to its comparatively long life (it decays to half value in about 3.85 days) this emanation is more easily investigated than that from thorium which decays to half value in less than one minute. Radium emanation is itself radio-active. It gives off  $\alpha$ -particles changing into a substance, radium A, which being solid is deposited on the walls of the vessel containing the gas.

**129 Elementary nature of radium emanation.** Radium emanation, though formed from radium, is itself an element. This is shown by its characteristic spectrum, which differs equally from that of radium as from the spectra of all other elements. The spectrum can easily be obtained by passing a little of the emanation into a small discharge tube. The colour of the discharge is bluish, and shows numerous bright lines differing from those of all other elements.

Since the emanation is formed from radium by the expulsion of an  $\alpha$ -particle of mass 3.99 its atomic weight should be about 222.5, taking that of radium as 226.5. The matter has been investigated directly by Ramsay and Gray, who succeeded in determining the density of the emanation using a quartz microbalance of special construction. For details of this brilliant piece of experimental work reference should be made to the original paper. The principle of the balance is simple. Two bulbs of very unequal size but of equal mass are placed at the two ends of the beam of a small quartz balance enclosed in a small air-tight chamber. The weights are adjusted so that the beam is horizontal when the balance case is completely evacuated. If gas is now admitted to the space around the balance the buoyancy of the gas will reduce the effective mass of the larger bulb, and thus cause a deflection of the beam.

The buoyancy of the gas can be calculated in terms of the deflection of the beam when the sensitivity of the balance is known, and from the buoyancy the density of the gas can be at once determined

The mean result of several experiments showed that the density of the emanation was 111.5 times that of hydrogen. This gives a molecular weight to the emanation of 223. The chemical properties of the gas resemble those of the argon group, and it is thus presumably monatomic. In this case its atomic weight is also 223. Considering that the total weight of the emanation available for the experiment was no more than 1/1000 of a milligram the agreement with the theoretical value is surprisingly good.

The emanation has been found to behave as a gas at ordinary temperatures. It obeys Boyle's law, it liquefies at  $-65^{\circ}\text{C}$  at normal pressure, but exerts an appreciable vapour pressure down to a temperature of  $-150^{\circ}\text{C}$ . According to Ramsay and Gray its critical temperature and pressure are  $104.5^{\circ}\text{C}$  and 63 atmospheres respectively. The density of the emanation at the temperature of liquid air, at which it is probably solid, is between 5 and 6.

Radium emanation is thus a definite chemical element belonging to the group of inert gases. Sir W. Ramsay proposed to emphasize this fact by giving it a separate name, Niton. The proposal, although desirable, has not met with general acceptance.

**130. Rate of decay of radium emanation.** As radium emanation is extensively used in experimental researches it is necessary to know its rate of decay with some accuracy. The simplest method is to allow the emanation in a closed tube to attain radio-active equilibrium with its immediate products radium A, B and C. These products are all short-lived, the most stable having a half period value of 26.8 minutes. A few hours thus suffices to set up transient equilibrium in the system. The rate of decay of any part of the activity is then, as we have already seen (§ 126), that of the most stable of the constituents, in this case the emanation. The advantage of this method is

that it allows us to use the  $\beta$ - and  $\gamma$ -rays, which, as we shall see later, are actually emitted by its disintegration products, radium B and radium C, as a measure of the activity of the emanation itself. It further allows us to evade the complications due to the growth of these products in the emanation during the first few hours after separation.

The apparatus used by Curie is shown in Fig. 102. The radium emanation, enclosed in a sealed glass tube *A*, is placed inside the brass tube *B*, which can be connected to a battery of cells and forms one plate of the ionization chamber. The

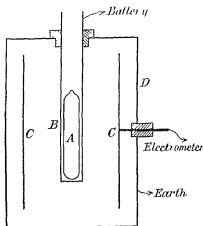


Fig. 102

insulated plate *C* takes the form of a cylinder concentric with *B*, and is connected in the usual way to an electrometer. The whole is surrounded by a metal chamber *D* which is earthed and serves to screen *C* from electrostatic disturbances. If *D* is made perfectly air-tight, changes in the current owing to fluctuations in the temperature and pressure of the atmosphere are avoided. The  $\alpha$ -rays due to the emanation itself are of course completely absorbed by the glass tube *A* and the metal tube *B*. The current is due to the  $\beta$ - and  $\gamma$ -rays from the radio-active decomposition products of the emanation. After a few hours these decay with the period of the emanation.

In this way the radio-active constant of the emanation was

found to be  $0.1801 \text{ (day)}^{-1}$  or  $2.085 \times 10^{-6} \text{ (sec.)}^{-1}$ . Rutherford by a different method obtained a value  $0.1802 \text{ (day)}^{-1}$ . The value of  $\lambda$  may thus be regarded as known to approximately one part in a thousand. It corresponds to a half value period of 3.85 days.

**131. Rate of escape of the emanation.** The rate of production of the emanation is simply proportional to the quantity of radium present. It follows the usual radio-active laws, and is independent of conditions. The rate at which the emanation escapes from the radium is, however, quite a different matter and depends very largely on conditions. If the compound is solid the greater part of the emanation is occluded by it. The amount occluded depends on the nature of the salt, and the area of it which is exposed to the air. A considerable fraction of the emanation escapes from a thin layer, much less from a thick one. The bulk of the occluded emanation is given off if the salt is dissolved, especially if an air is bubbled through the solution. The rate of escape is also much increased by raising the temperature. The rate of escape of the emanation can be increased forty times by raising the temperature from  $-80^\circ$  to  $800^\circ \text{ C}$ . The rate of production is, however, constant throughout the range, the difference being that at the low temperatures the emanation disintegrates within the substance, while in the latter it is given off into the space above the radium before disintegrating. Similar results are obtained with thorium and thorium emanation.

**132. Measurement of the volume of the emanation in equilibrium with one gram of radium.** The quantity of emanation in radio-active equilibrium with one gram of radium is by the laws of radio-active change a definite amount. It is termed a *curie*. Since the curie is a somewhat large standard compared with the amounts of emanation generally available for experimental purposes one-thousandth part of this is taken as a subsidiary standard and is known as the *millicurie*. The value of the curie can be estimated from the radio-active constants. It has been found by the method of § 103 that one

gram of pure radium (free from its products) emits  $3.4 \times 10^{10}$   $\alpha$ -particles per second. As each atom of radium disintegrates into one atom of emanation with the expulsion of one  $\alpha$ -particle this is also the number of emanation atoms formed per second. But the number present when equilibrium is reached is equal to  $q/\lambda$  where  $q$  is the rate of formation of the atoms, and  $\lambda$  the radio-active constant of the emanation. The total number of atoms of emanation in equilibrium with one gram of radium is thus

$$3.4 \times 10^{10} / 2.085 \times 10^{-6} = 1.63 \times 10^{16}$$

Since there are  $2.78 \times 10^{20}$  molecules in one c.c. of gas at normal temperature and pressure the volume occupied by one curie of emanation under these conditions is

$$1.63 \times 10^{16} / 2.78 \times 10^{20} \text{ c.c.} = 0.59 \text{ cubic mm.}$$

This value has been confirmed by direct experiment, the purified emanation from a known weight of radium being passed into a calibrated capillary tube. The observed value agreed closely with that calculated, again affording further proof of the correctness of the principles involved.

**133. The active deposit from radium emanation.** If a plate or wire of any kind is exposed to radium emanation for a few hours and then withdrawn it is found to have become radio-active, the more concentrated the emanation the greater the activity. This phenomenon was at first described as induced or excited activity. It is now known to be due to the deposition on the surface of the substance of a radio-active product due to the decomposition of the emanation.

If the wire is allowed to remain in the emanation sufficiently long to attain equilibrium the amount of the activity is independent of the position or material of the plate, and is strictly proportional to the amount of emanation present. It is also directly proportional to the area of the surface exposed.

A curious property of the excited activity is that it can be concentrated on a very small area if the latter is charged negatively. Thus if a wire *B* (Fig. 103) is passed into a metal chamber *A* containing a radium compound, and charged to a high potential, the activity when the charge on the wire is

negative is as much as 200 times its activity when positively charged. In this way practically the whole of this "excited" activity can be concentrated on the wire, which may be made to have an activity per unit area of over 10,000 times that of the surface of the radium itself.

Since the activity is concentrated on the negative electrode the carriers of the activity must have a positive charge. Since the active deposit is formed from the emanation by the emission of a positive particle carrying two electronic charges we should have expected the residual atom to have been negatively charged. We know, however, that the impact of a positive particle on matter gives rise to a number of slow-moving electrons, or  $\delta$ -rays as they have been called. It seems evident,

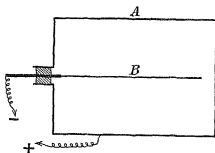


Fig 103

therefore, that the escape of a positive ray from an atom must also be attended by an emission of negative electricity, probably in the form of these slow-moving electrons. Since the residual atom has a positive charge it is evident that at least three such electrons must be expelled with each positive particle.

These positively charged carriers move under the electric field in the same way as the ions in a gas, and similarly lose their charges owing to recombination with the negative ions in the gas. Thus if the potential of the negative electrode is gradually increased the activity on the electrode increases in almost exactly the same way as the current through an ionized gas, the activity reaching a constant maximum when the field is sufficiently large to convey all the carriers to the negative electrode before any appreciable recombination has taken place.

The velocity of the carriers in an electric field can be measured by methods analogous to those used to determine the mobilities of the ions. Their velocity in a field of one volt per cm. is about 1.1 cm. per sec. or very nearly that of the positive ion in a gas. There is some evidence for the assumption that they carry a single negative charge.

**134. Recoil atoms** The  $\alpha$ -particle is expelled from the emanation atom with considerable velocity. The residual atom itself must thus be projected in the opposite direction with a velocity which is given by the consideration that the momentum of the system as a whole must be zero. Since the mass of the  $\alpha$ -particle is 4, and that of the residual atom ( $222 - 4$ ), the velocity of the recoil atom will be  $1/218$  or about  $1/55$  of that of the corresponding  $\alpha$ -particle. These recoil atoms as they are termed are brought to rest in passing through a gas in exactly the same way as the  $\alpha$ -particles. Owing to their much smaller velocity, however, their range is considerably less.

Owing to the high kinetic energy of the recoil atoms the electric field has little effect upon them until they have been reduced to rest by the surrounding gas. They then behave as ordinary charged ions and are dispatched to the negative electrode. Hence if the pressure in the vessel is reduced so low that the recoil atoms can reach the walls of the vessel before coming to rest the distribution of the activity will be uninfluenced by an electric field, the cathode having no larger share of the activity than the rest of the chamber, and the activity is then uniformly distributed. This has been shown to be the case experimentally, the pressure at which it occurs in ordinary sized vessels being of the order of 1 mm. The range of the recoil atoms, as of the  $\alpha$ -particles, is directly proportional to the pressure of the gas. Thus the range of the recoil atoms can be deduced by the method described in § 104. It is found to be about 0.12 mm. in air at atmospheric pressure and about 0.7 mm. in hydrogen. The velocity of the recoil atoms has been measured directly, and found to be in good agreement with that deduced from a consideration of the range, and with that to be expected from the theory of their origin stated above.



### 135 Analysis of the active deposit of rapid change

A body which has been exposed to radium emanation is found after removal from the emanation to give out all three kinds of radiations. The activity is comparatively short-lived and almost completely disappears within 24 hours after withdrawal from the emanation. There is, however, always a small residual activity which if the body has been exposed to emanation for several days may reach as much as one-millionth of the initial activity, and the activity of this portion is found to increase steadily with time over the space of several years.

We may therefore for convenience divide the excited activity into two parts, (1) the active deposit of rapid change, (2) the active deposit of slow change. Since the activity of the latter is in general minute compared with that of the former, we may neglect the small residual effects due to it in our analysis of the short-lived deposit.

For experimental purposes it is convenient to obtain the deposit on a wire or thin rod. This may be done in the apparatus shown in Fig. 103. The central wire *B* is raised to a high negative potential, and radium emanation is passed into the apparatus. The bulk of the active deposit collects on the negative wire *A*. If the activity is to be measured by the  $\alpha$ -rays the rod may then be made the central electrode of a cylindrical ionization chamber, the saturation current being measured by an electrometer in the usual way. If  $\beta$ - or  $\gamma$ -rays are to be used to measure the activity a simple electroscope of the type described in § 120 (Fig. 97) is convenient. If  $\beta$ -rays are to be employed the opening of the electroscope is covered with only sufficient thickness of aluminium foil to absorb all the  $\alpha$ -rays. If only  $\gamma$ -rays are to be dealt with the electroscope may be placed on a sheet of lead some half centimetre in thickness, which will cut off every thing except the  $\gamma$ -rays.

The shape of the decay curves depends on whether the  $\alpha$ - or the  $\beta$ -rays are used for the measurement, and also on the time of exposure of the wire to the emanation. The active deposit consists therefore of a mixture of radio-active substances, all in the solid state, some emitting  $\alpha$ -rays, and some  $\beta$ - and  $\gamma$ -rays only.

The decay curve obtained after a short exposure of the wire

to the emanation, and measured by the  $\alpha$ -ray activity, is shown in Fig. 104. It will be seen to be divisible into three parts. The first stage shows a rapid decay falling to some 10 per cent. of its initial value in 15 minutes. This is followed by a period of some 20 minutes in which there is little variation in the activity. Then a gradual exponential decrease follows, the curve falling to half value in about 28 minutes.

Since the exposure was short the initial substance consisted almost entirely of the first decomposition product of the

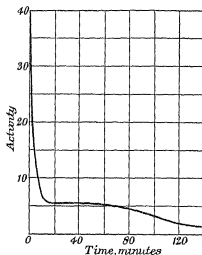


Fig. 104 Decay of excited activity,  $\alpha$  ray curve

emanation which we will call radium A. An analysis of the first part of the decay curve shows that this substance emits  $\alpha$ -particles and decays to half value in about three minutes, giving rise to a product which emits  $\alpha$ -rays and decays with a half value period of 28 minutes.

Further evidence on the nature of the changes can be obtained from a study of the  $\beta$ -ray curves. The  $\beta$ -ray curves for short and long exposures are shown in the curves of Fig. 105. The curve for a short exposure of one minute shows that the  $\beta$ -ray activity is initially absent, and that therefore radium A emits only  $\alpha$ -rays. If, however, the product emitting the  $\beta$ -rays was

the immediate product of the decomposition of the radium A, the curve for the rise of activity of the  $\beta$ -ray product should be (neglecting the decay of the latter) complementary to the decay curve of radium A, that is, it should rise to half value in about three minutes. As a matter of fact the rise to half value occupies rather more than ten minutes and a substitution of the numerical values in the formulae shews that this discrepancy cannot be explained by the small decay of the  $\beta$ -ray product in that interval of time. We are thus led to the conclusion that there is between the radium A and the  $\beta$ -ray product another radio-active substance which we will term radium B, which

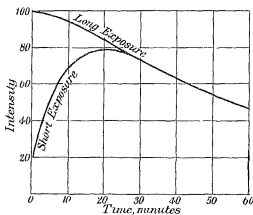


Fig. 105

without itself emitting ionizing rays gives rise to the product radium C which does

The period of the two products radium B and C can best be obtained from a study of the curves obtained for the  $\beta$ -ray activity with long exposure. In this case the three products will be in radio-active equilibrium, and the relative amount of the short-lived radium A will consequently be very small. Moreover as it has a short period it will rapidly cease to affect the shape of the decay curves. The whole of the radium A (except one per cent) is, in fact, disintegrated within twenty minutes after removal from the emanation and the curve is then due solely to radium B and C.

Now it is found that this curve can be accurately expressed by an empirical formula of the form

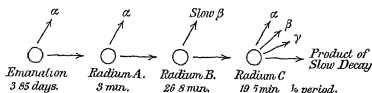
$$I_1/I_0 = a e^{-\lambda t} = (a - 1) e^{-\lambda t} \quad (117)$$

where  $\alpha$  is a numerical constant and  $\lambda_3$  and  $\lambda_2$  have the values  $5.38 \times 10^{-1}$  and  $4.13 \times 10^{-1} (\text{sec})^{-1}$  respectively. It will be seen that the second of these gives a half value period of 28 minutes, the other a half value period of about 20 minutes.

Now we have already seen that the final rate of decay will be governed by the decay of the substance of longest period, irrespective of its position in the chain of decomposition. Hence we cannot immediately infer to which of the substances B or C the two constants refer.

Fortunately, however, it is possible to separate the two products. If the wire is heated to a temperature of some 600° C. surrounded by a cooled outer cylinder it is found that the activity can be separated into two parts, one part remaining on the wire while the other part is volatilized and condenses on the cool outer cylinder. The portion remaining on the wire emits  $\alpha$ -radiation and  $\beta$ -radiation, the activity in each case falling to half value in 19.5 minutes. The other portion is initially inactive but gradually begins to emit both  $\alpha$ - and  $\beta$ -rays corresponding to those of the substance left behind on the wire. The shorter period therefore corresponds with the final product, radium C, which emits both  $\alpha$ - and  $\beta$ -rays, while the longer period 26.8 minutes is that of the radium B which without emitting radiations is the direct parent of the radium C and the immediate product of the decomposition of radium A.

The series of changes with which we are dealing can thus be represented by the following chain



It has been found that the change from radium B to radium C is not entirely rayless. A quantity of slowly-moving  $\beta$ -particles comparable with the  $\delta$ -rays are given off. These, however, have so little penetrating power that they are completely absorbed in the thickness of aluminium necessary to cut off the  $\alpha$ -rays. Under the conditions under which the  $\beta$ -ray curves are generally measured they are therefore unable to enter the ionization chamber and hence exercise no effect on the shape of the curves for the  $\beta$ -ray activity. It is possible that all the changes described as rayless are really of this nature.

The theoretical shape of the various decay curves can be deduced from equations similar to those in § 126 since the various radio-active constants are known.

In order to test the adequacy of the disintegration theory the theoretical decay curves for the cases we have just been considering have been drawn by Rutherford, and compared with the decay curves obtained by actual experiment. The agreement of the two sets of curves was most satisfactory, the discrepancy being in general no more than one per cent. The theory of radio-active disintegration contained in the propositions in § 125 is thus completely adequate to explain even such complicated cases of radio-active change as those we have been discussing.

**136 Separation of the products by the method of "recoil."** Complex nature of radium C. Although the analysis of the radio-active product of short period was made in the manner explained above we have now a more powerful means of separating the various products of radio-active change. This can be done by making use of the "recoil" atoms already described. We have seen that the atom of radium A produced by the decomposition of radium emanation starts life with a velocity which will enable it to travel across several centimetres of gas at a sufficiently low pressure. The same considerations apply also to the atoms formed by the decomposition of radium A and indeed to any atoms whose formation is attended by the expulsion of an  $\alpha$ -particle. Thus if we place the wire or plate carrying the induced activity in a vacuum at

a short distance from another inactive plate, the atoms of radium B formed by the decomposition of radium A will in many cases be shot across the intervening space, and collect on the inactive plate. In this way radium B of considerable purity can be obtained, since the atoms of radium C, which are formed from radium B with the emission of slowly moving  $\beta$ -particles only, have no appreciable velocity. The radium C thus remains on the active plate. The individual properties of the separate substances can thus be studied.

An application of this method to the case of radium C has led to interesting results. Most radio-active atoms disintegrate with the emission of either  $\alpha$ -rays or  $\beta$ - and  $\gamma$ -rays but not both. Radium C, as we have noted, gives all three types. Pure radium C can be obtained from the radio-active deposit of radium emanation by dissolving it in acid, and suspending a nickel plate in the solution. The radium C is deposited on the plate, leaving the radium B in solution. It must be remembered that each radio-active product is an element with definite chemical properties, and differs from ordinary elements only in its instability. The various products can thus be separated by the usual methods of chemical analysis. If the nickel plate bearing the radium C is placed in vacuo near a negatively charged disk recoil atoms from the radium C collect on the disk, which thus becomes radio-active. It is found, however, that the properties of the radio-active substance thus collected are quite distinct from those of the normal product of the disintegration of radium C (which is known as radium D). Thus it has a half value period of 138 minutes as against 16 years for radium D. This new substance which has been called radium C<sub>2</sub> gives out only  $\beta$ - and  $\gamma$ -rays of the same quality as those of radium C. Further, it does not give rise to radium D on disintegration.

We have here a case (the first one actually observed although others have now been recorded) in which a branch occurs in the radio-active chain. Radium C splits up in two different ways, the normal disintegration gives rise to radium D and its products in the normal line of descent, but a certain fraction of the atoms (about 1 in 6000) break up in a different way giving rise to this new product, radium C<sub>2</sub>, the disintegration

product of which is not radio-active and is probably lead (§ 142) These exceptions to the usual rule are of great interest, as they may possibly throw some light on the mysterious question of the origin of radio-active change

**137 The radio-active product of slow change** As we have seen, radium C normally breaks up with the expulsion of an  $\alpha$ -particle into a product radium D. Radium D marks a period of comparative quiescence in the radio-active decay, its half value period being about 16.5 years. Owing to its long period it is present in minute but appreciable quantities in ores containing radium from which it can be separated by the chemical processes used for the separation of lead, to which metal indeed it bears so close a resemblance that no chemical test has yet been devised for distinguishing between them. Radium D gives out neither  $\alpha$ - nor  $\beta$ -rays of the ordinary type. It has, however, been shewn to give off very slow  $\beta$ -rays (or  $\delta$ -rays) of the type given off by radium B.

The succeeding product, radium E, gives off  $\beta$ - and  $\gamma$ -rays and has a period of five days. The relation between radium D and its immediate product is thus the same as that for uranium and uranium X, and the decay and recovery curves follow the same laws. Thus in freshly prepared radium D the  $\beta$ -ray activity rises according to equation (106) to a maximum which owing to the slow decay of radium D remains sensibly constant for a considerable time.

Radium F, the product of the decay of radium E, emits  $\alpha$ -rays and decays to half value in 136 days. Its rate of decay and the range of its  $\alpha$ -particles identify it with the substance polonium, the first radio-active substance actually isolated from pitchblende. The product of the disintegration of polonium is apparently not radio-active, no trace of any radiations being observed after the  $\alpha$ -ray activity of the polonium has disappeared. The final product of the chain has with much probability been identified with lead.

The period of radium D is too long to be determined by direct measurements. It can, however, be deduced by indirect methods which form an interesting illustration of the principles

we have been discussing. Suppose we commence with a definite quantity of emanation, say, one millicurie. The number of atoms of emanation present is then known from the determination of the curie already discussed (§ 132). Let it be  $N$ . The number of atoms of emanation breaking up per second at the beginning of the experiment is therefore  $\lambda_1 N$ , where  $\lambda_1$  is the radio-active constant of the emanation. This will be the number of  $\alpha$ -particles  $n_1$ , emitted per second by the emanation present, a quantity which we can determine by the method already described (§ 103).

The emanation is then allowed to decay for a month or so at the end of which time it is practically all in the form of radium D. The number of atoms of radium D present is thus the same as the number of atoms of emanation with which we started, that is  $N$ , and the number breaking up per second is therefore  $\lambda_2 N$  where  $\lambda_2$  is the radio-active constant of radium D. Now radium D itself emits no  $\alpha$ -particles. As, however, the period of radium D is long compared with that of its products E and F, the latter will be in radio-active equilibrium with it and hence the number of radium F particles breaking up per second will be the same as the number of radium D atoms disintegrating in the same time, that is  $\lambda_2 N$ . But this is the number  $n_2$  of  $\alpha$ -particles emitted per second by the mixture of radium D, E, and F in our tube, since D and E give no  $\alpha$ -radiation. Hence

$$\frac{\lambda_2 N}{\lambda_1 N} = \frac{n_2}{n_1},$$

from which we can determine  $\lambda_2$  since all the other quantities are known. The value of  $\lambda_2$  is found to be  $0.042 \text{ (year)}^{-1}$ , corresponding to a half value period of 16.5 years.

**138 The radio-activity of thorium and actinium** The element thorium is radio-active and gives rise to a chain of radio-active products in the same way as uranium gives rise to the radium chain. The disintegration process can be studied in detail by the methods already discussed, and involves no new principles. The results are sufficiently summarized in Table XI. For further details Rutherford's *Radio-active Substances and their Radiations* may be consulted.



A new element, actinium, also gives a radio-active chain of products.

TABLE X  
Uranium-Radium series

SUBSTANCE	Radio-active constant $\lambda$ in (sec) <sup>-1</sup>	Half value period	Radiations emitted	Range of $\alpha$ particles in air in cm.
Uranium I	$4.3 \times 10^{-18}$	$5 \times 10^8$ years	$\alpha$	2.37
↓ Uranium Y	$5.4 \times 10^{-6}$	1.5 days	$\beta$ (slow)	—
Uranium X <sub>1</sub>	$3.3 \times 10^{-7}$	24.6 days	$\beta$ (slow)	—
Uranium X <sub>2</sub>	$1.0 \times 10^{-2}$	1.15 min	$\beta$	—
Uranium 2	$1 \times 10^{-14}$	$2 \times 10^4$ years	$\alpha$	2.75
Thorium	$1 \times 10^{-13}$	$2 \times 10^8$ years	$\alpha$	2.85
Radium	$1.26 \times 10^{-11}$	1730 years	$\alpha$	3.13
Radium emanation	$2.085 \times 10^{-6}$	3.85 days	$\alpha$	3.94
Radium A	$3.85 \times 10^{-3}$	3.0 min	$\alpha$	4.50
Radium B	$4.33 \times 10^{-1}$	26.7 min	$\beta$ (slow)	—
Radium C*	$5.93 \times 10^{-4}$	19.5 min	$\beta$	—
↓ Radium C <sub>2</sub>	$8.3 \times 10^{-3}$	1.4 min	$\beta$	—
Radium C <sub>1</sub>	—	$10^{-6}$ sec	$\alpha$	6.57
↓ Radium D	$7.3 \times 10^{-9}$	16.5 years	$\beta$ (slow)	—
Radium E	$1.6 \times 10^{-6}$	5.0 days	$\beta$ (slow)	—
Radium F (Polonium)	$5.90 \times 10^{-8}$	136 days	$\alpha$	3.58
Lead	—	—	—	—

\* The production of radium C<sub>1</sub> from radium C is attended by the expulsion of a  $\beta$  particle only. The expulsion of an  $\alpha$ -particle from radium C produces radium C<sub>2</sub>. As thus a particle gives rise to the branch series only, it is omitted from the table to avoid confusion.

It may be noted that very careful analysis has shewn that the disintegration of uranium is considerably more complex

TABLE XI  
Thorium and Actinium Series

SUBSTANCE	Radio active constant $\lambda$ in (sec) <sup>-1</sup>	Half value period	Radiations emitted	Range of $\alpha$ particles in air in cm
Thorium	$1.2 \cdot 10^{-18}$	$1.8 \cdot 10^{10}$ years	$\alpha$	2.58
Mesothorium 1	$4.0 \cdot 10^{-9}$	5.5 years	—	—
Mesothorium 2	$3.1 \cdot 10^{-5}$	6.2 hours	$\beta$	—
Radiothorium	$1.09 \cdot 10^{-8}$	2.0 years	$\alpha$	3.67
Thorium X	$2.20 \cdot 10^{-4}$	3.61 days	$\alpha$	4.08
Thorium emanation	$1.28 \cdot 10^{-2}$	54 sec	$\alpha$	4.74
Thorium A	5.0	0.11 sec	$\alpha$	5.40
Thorium B	$1.8 \cdot 10^{-1}$	10.6 hours	$\beta$ (slow)	—
*Thorium C	$1.9 \cdot 10^{-1}$	60 minutes	$\alpha, \beta$	4.55
↓ Thorium C <sub>1</sub>	$3.7 \cdot 10^{-1}$	3.1 minutes	$\beta$	—
↓ Thorium C <sub>2</sub>	$7 \cdot 10^{10}$	$10^{-11}$ sec.	$\alpha$	8.16
↓ Lead				
Uranium Y	$5.4 \cdot 10^{-1}$	1.5 days	$\beta$ (slow)	—
Proto-actinium	?	10 000 years	$\alpha$	—
Actinium	—	30 years	$\beta$	—
Radioactinium	$1.1 \cdot 10^{-7}$	19.5 days	$\alpha$	4.36
Actinium X	$7.6 \cdot 10^{-7}$	11.4 days	$\alpha$	4.17
Actinium emanation	$1.8 \cdot 10^{-1}$	3.9 sec	$\alpha$	5.40
Actinium A	350	60.2 sec	$\alpha$	6.16
Actinium B	$3.2 \cdot 10^{-1}$	36.1 min	$\beta$ (slow)	—
*Actinium C	$5.37 \cdot 10^{-1}$	2.15 min	$\alpha, \beta$	5.12
↓ Actinium C <sub>1</sub>	—	—	$\beta$	—
↓ Actinium C <sub>2</sub>	$2.26 \cdot 10^{-1}$	4.71 min	$\alpha$	—
↓ Lead				

\* The  $C \rightarrow C_1$  transformation is attended by the expulsion of a  $\beta$ -particle only, that from  $C \rightarrow C_1$  by the expulsion of an  $\alpha$  particle

than we have described in the previous chapter. Uranium in fact contains two radio-active substances which can be differentiated by a slight difference in range of the  $\alpha$ -particles which they emit. The disintegration of uranium 1 has been found to be complex, a small quantity of a new product, uranium Y, being formed, in addition to the uranium X. There is thus a branching of the chain at uranium resembling that already described for radium C. This branch series has been shown to give rise to the element actinium, one other radio-active substance (proto-actinium) of long, but as yet undetermined, period intervening. The relationship is sufficiently indicated in Table XI.

**139 Position of the radio-active elements in the Periodic Table.** The influx of the large number of new elements tabulated in the preceding section seemed likely seriously to overload the corresponding portion of the table of the periodic classification of the elements and the exact relation of the new elements to each other and to the non-radio-active elements of similar atomic weight gave rise to much discussion. Since an  $\alpha$ -particle has been shown to be an atom of helium, the emission of an  $\alpha$ -particle obviously produces a new atom with an atomic weight of four units less than that of the atom from which it was formed. On the other hand, the emission of a  $\beta$ -particle makes no sensible change in the atomic weight. Thus uranium 1 with an atomic weight of 238 loses an  $\alpha$ -particle and changes into uranium  $X_1$  which must thus have an atomic weight 234. The emission of a  $\beta$ -particle leaves the atomic weight unchanged so that 234 is also the atomic weight of both uranium  $X_2$  and uranium 2. Similarly, the atomic weight of ionium must be 230, that of radium 226, and that of radium emanation 222. The two last results have, as we have seen, been verified by direct determination, thus proving the accuracy of the reasoning adopted. The final product of the uranium and actinium series should thus have an atomic weight of 206 in each case, and that of the thorium series an atomic weight of 204. We have thus some 35 new elements to arrange in the nine spaces which occur in the periodic table between lead and uranium.

From a study of so much of the chemical behaviour of the radio-active elements as could be observed, Soddy suggested that the emission of an  $\alpha$ -particle by a radio-active element produced a new element whose position in the table was two spaces to the left of that of the element from which it was formed. The emission of a  $\beta$ -particle moved the position of the new element one space to the right. Thus the emission of an  $\alpha$ -particle by uranium 1, which is placed in group VI of the periodic table, produces a new element uranium  $X_1$  which should be placed in group IV of the table. Uranium  $X_2$ , formed from uranium  $X_1$  by the emission of a  $\beta$ -particle only, would then occupy a position in group V, although its atomic weight is identical with that of uranium  $X_1$ , and similarly uranium 2, also of the same atomic weight, is placed in group VI in the same space in the table as the original uranium 1, though differing from the latter in atomic weight by four units. The fact that uranium 1 and uranium 2 are inseparable by any chemical process gives weight to the assumptions.

Similarly it is found that the three radio-active emanations occupy the same space in the table, in the group of the inert gases, to which they obviously belong.

Substances occupying the same space in the periodic table, and thus presumably having identical chemical properties, though differing in their mode of disintegration and atomic weight, were called *isotopes*. The later discovery of Aston (§ 58) that many of the ordinary "pure" chemical elements were in reality mixtures of two or more substances of different atomic weight has placed the correctness of Soddy's suggestion beyond dispute. Rutherford's theory of the atomic nucleus (§ 147) affords, as we shall see, a complete theoretical explanation of the effects.

The appended table shews Soddy's classification for the whole of the elements in the uranium-radium series, and the initial portion of the actinium series as far as actinium emanation. To avoid confusion the latter portion of the actinium series, and the whole of the thorium series, have been omitted.

TABLE XII  
Classification of Radio-active Elements

At Wt	0	I	II	III	IV	V	VI	VII
206					Radio Lead			
210				RaC <sub>2</sub>	RaD	RaE	RaF	
214					RaB	RaC	RaC <sub>1</sub>	
218	Ac Em						RaA	
222	RaEm		AcX					
226			Ra	Ac	RaAc			
230					Io	UY	PA	
234					UX <sub>1</sub>	UX <sub>2</sub>	U <sub>2</sub>	
238							U <sub>1</sub>	

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## GENERAL

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## CHAPTER XV

### SOME PROBLEMS IN RADIO-ACTIVITY

140. **Uranium and the origin of radium.** That the origin of radium was to be found in uranium was long suspected. It is obvious that since radium decays to half value in less than 2000 years it would no longer exist on the earth at the present day unless it were being continually formed from some more stable substance. The constant association of radium with uranium ores and the radio-activity of the latter element naturally led to the supposition that radium was formed by the disintegration of the uranium atom.

The observed constancy of the ratio of the radium to the uranium in uranium ores of very varied composition strongly supported this assumption. The constancy of the ratio is, indeed, very remarkable, the only exceptions being in the case of minerals which are known from geological evidence to have been comparatively recent deposits (in which case radio-active equilibrium will not have been established) or to have been subjected to the action of water or other disintegrating circumstances.

While this proves that radium is a member of the uranium disintegration series it does not follow that it is the direct product of the decomposition of uranium X. In fact it is quite easy to shew that this is not the case. The transformation constant of uranium is  $4.3 \times 10^{-18}$  secs. or  $1.4 \times 10^{-10}$  years. As an atom of uranium of atomic weight 238 produces one of radium with an atomic weight 226, the total weight of radium formed in one year from a kilogram of pure uranium should, if the uranium changes directly into radium, be

$$1000 \times (1.4 \times 10^{-10}) \times 226/238$$

or  $1.3 \times 10^{-7}$  gm. This could be detected with ease. In fact even one-thousandth part of this could be detected with some

certainty. On making the experiments it was found that commencing with pure uranium (free from all its radio-active products) the rate of production of radium was certainly less than one-thousandth part of what would be expected if uranium X changed directly into radium. There must therefore be some product of long period intermediate between these two members of the chain.

Two intermediate substances have now been isolated. One is known as ionium. It has a period which is estimated at about  $2 \times 10^3$  years, and gives off  $\alpha$ -particles of comparatively small range. It is chemically similar to thorium, but differs from it in the range of the  $\alpha$ -particles and in its radio-active constant. The production of radium in solutions of ionium has been observed. The other is known as Uranium 2, and has a period of  $2 \times 10^5$  years.

**141 Production of helium from uranium.** Geological age. Since each  $\alpha$ -particle is an atom of helium, helium must be in process of formation in all minerals containing uranium. The number of  $\alpha$ -particles given out by one gram of uranium in equilibrium with all its products has been found to be  $9.7 \times 10^4$  per second. The number of atoms of helium formed per annum by one gram of uranium is thus

$$(9.7 \times 10^4) \times 60 \times 60 \times 24 \times 365$$

or taking Avogadro's constant as  $2.7 \times 10^{19}$  molecules per c.c., about  $11 \times 10^{-5}$  cubic mm. The direct measurement of the rate at which helium is produced in uranium ores is in fair agreement with this estimate.

Thus if we can assume that the helium produced is all occluded by the mineral, the ratio of the helium to the uranium present affords us a method of estimating the age of the mineral. The results are found to be qualitatively consistent with the ages suggested by geological considerations, that is to say, the rocks of older formations give a higher ratio of helium to uranium than those of more recent formation. Strutt, to whom most of our information is due, estimates the age of the oligocene rocks as eight million years, and the ages of the eocene, carboniferous, and archæan periods as respectively

31, 150 and 700 million years. Since there is always the possibility of a certain loss of helium from the rocks by diffusion into the air, these are obviously minimum estimates.

**142 The end-product of the uranium chain.** Polonium is the last radio-active member of the uranium-radium series. After the decay of the polonium no residual activity of any kind has been discovered. As we have seen the atomic weight of the final product should be about 206, approximately that of lead (207). If this is so, there should be some definite constant ratio between the amount of lead present in a uranium ore and the quantity of helium also present. For the formation of one atom of lead by the disintegration of an atom of uranium is attended with the emission of eight atoms of helium each of atomic weight 4. Hence the mass of lead present should be  $206/(8 \times 4)$  or 6.5 times that of the helium present supposing both to be formed by the disintegration of uranium.

The observed ratios vary considerably in different minerals. This is to be expected since in the first place helium may escape through diffusion from the mineral, while in the second place lead may have been originally present in the mineral apart from its uranium content, as lead is a somewhat widely diffused element. In general the ratio of lead to helium is about twice the calculated value. Under the circumstances the agreement is sufficiently satisfactory, and the production of lead by the disintegration of uranium may be regarded as reasonably certain.

Assuming lead to be also the last product of the thorium chain, its atomic weight should be  $232 - 24$  or 208, since the disintegration is attended by the expulsion of six  $\alpha$ -particles. It is interesting to note that the atomic weight of the lead extracted from radio-active minerals has now been determined by purely chemical methods. The "lead" from uranium ores gives an atomic weight of 206.1, that from thorium ores of about 208, both agreeing closely with the values deduced from radio-active theory. The atomic weight of "ordinary" lead falls between these two values. The latter is, therefore, probably a mixture of the two isotopes.

The ratio of lead to uranium may therefore be used as a



criterion of the age of the minerals. This will obviously give a maximum estimate. In this way the age of the carboniferous rocks has been calculated as about 340 million years, and of the archæan rocks as about 1300 million years. Their true age probably lies between these values and those given by Stauß from a study of the helium content.

**143 The heating effect of radium.** Since the various radiations from radio-active substances are emitted with very high velocities it is evident that a radio-active substance is giving out energy at a very appreciable rate. If it is surrounded by sufficient material to absorb all the radiations this energy will manifest itself eventually in the form of heat. Thus radium, for example, is constantly producing heat and will maintain itself at an appreciably higher temperature than its surroundings.

Owing to their relatively large mass the bulk of the energy is carried by the  $\alpha$ -rays. The percentage of energy carried by the  $\beta$ - and  $\gamma$ -rays is somewhat difficult to estimate exactly but is certainly small. The total number of ions formed in air by the complete absorption of the  $\beta$ -rays from a gram of radium is estimated at  $9 \times 10^{14}$ , and by the  $\gamma$ -rays at  $13 \times 10^{14}$ . The number of ions produced by the  $\alpha$ -rays from the same source is  $2.56 \times 10^{16}$ . If we assume that these numbers are approximately proportional to the energy in the rays, these results shew that about 8 per cent. of the energy is associated with the  $\beta$ - and  $\gamma$ -radiations.

The heating effect of the  $\alpha$ -rays can be calculated from their known velocities. Let  $n$  be the number of  $\alpha$ -particles of velocity  $v$  emitted per second by each of the  $\alpha$ -ray products present;  $n$  will be the same for each if equilibrium is established. The total energy of the  $\alpha$ -rays is thus  $\frac{1}{2}m\Sigma nv^2$  where  $m$  is the mass of an  $\alpha$ -particle. To this we must add the energy of recoil of the various recoil atoms which as we have seen is  $m/M$  of that of the corresponding  $\alpha$ -particle, where  $M$  is the mass of the recoil atom. Thus the total energy associated with the  $\alpha$ -radiation is

$$\frac{1}{2}mn\Sigma\left(1+\frac{m}{M}\right)v^2.$$

In the case of radium in equilibrium with its short period

products this is equal to  $1.38 \times 10^6$  ergs per second, or about 118 gram calories per hour. If only the  $\alpha$ -rays are absorbed in the apparatus this should be the rate of emission of heat by one gram of radium in equilibrium with its short lived products. If the radium has been prepared for several years so that an appreciable amount of polonium is present the heating effect of this must be added. If the apparatus, as is usually the case, absorbs an appreciable percentage of the  $\beta$ - and  $\gamma$ -rays the heating effect will be somewhat greater, if all the rays are absorbed it should be about 128 calories per hour.

The effect is thus quite measurable. The most sensitive form of apparatus for this purpose is that designed by Duane, following a suggestion of Callender's. It is shown in Fig. 106.

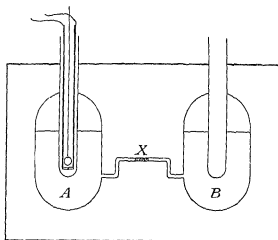


FIG. 106

The radio-active compound is placed in the bulb *A* of a sort of differential vapour pressure thermometer, which is connected to a second similar bulb *B*. Both bulbs contain a volatile liquid (ether, for example) but are carefully freed from air. A short liquid index *X* in the connecting tube shows the equality of pressure in the two bulbs.

Owing to the emission of heat by the compound in *A* the temperature in *A* would rise and thus the vapour pressure increase. As the vapour pressure of ether increases rapidly

with temperature the instrument is very sensitive to temperature changes. The heating effect is, however, counteracted by passing a current in the proper direction through a junction of bismuth and antimony. This produces an absorption of heat (Peltier effect) which is proportional to the current and is known if the coefficient of the Peltier effect for the two metals is known. By adjusting the current until the index remains stationary, the emission of heat by the compound is equal to the absorption of heat by the junction and is thus known if the current is measured. An emission of heat of 0002 calorie per second can be detected with certainty. The values obtained in this way vary between 120 and 132 calories per hour per gm., figures which agree sufficiently closely with the calculated values.

It has been found, using an apparatus of this sort, that in the case of such a substance as radium emanation the rate of emission of heat decays at the same rate as the substance itself. We can thus calculate the total heat emitted by a radio-active substance during its life. Taking the case of radium emanation, for example, it is found that one curie of emanation gives out 109 calories per hour. The mass of one curie is  $6 \times 10^{-6}$  gm., and hence the rate of emission of heat by the emanation is  $1.82 \times 10^7$  calories per hour per gm. But since the rate of emission decreases with the decay of the emanation we have

$$H = H_0 e^{-\lambda t}$$

where  $H$  is the rate of emission at the instant  $t$ . Thus the total heat emitted by the emanation is

$$\int_0^{\infty} H_0 e^{-\lambda t} dt = H_0 / \lambda$$

Now  $\lambda$ , the radio-active constant of the emanation, is  $2.085 \times 10^{-6}$  per sec. or .0075 per hour, and  $H_0$  has just been obtained. Hence the total heat emitted by a gram of emanation would be no less than  $1.82 \times 10^7 / 0.0075$ , or  $2.44 \times 10^9$  calories.

The formation of one gram of water is attended with the liberation of about  $3.8 \times 10^4$  calories of heat. This is the most energetic reaction known to chemists. It will be seen therefore that the heat liberated in any chemical reaction is infinitesimal compared with that produced by radio-active changes.

The change also differs from chemical action in the fact that it is independent of temperature. If a quantity of radium enclosed in a tube is lowered into liquid hydrogen, the rate of heat emission can be calculated by measuring the rate at which the liquid hydrogen is evaporated, the latent heat of liquid hydrogen being known. The experiment was performed by Curie and Dewar, and gave results comparable with the values obtained by other methods at ordinary temperatures. Thus even at the temperature of liquid hydrogen, a temperature at which even the most active chemical changes cease, the rate of emission of heat by the radio-active substance remains unaltered.

This energy must be derived from the internal energy of the atoms themselves. Since the radio-active elements differ in no way from non-active elements except for their instability the amount of intra-atomic energy must be very large. Thus the emanation gives out  $2.11 \times 10^9$  calories in changing from an atomic weight of 222 to one of 210 with the emission of three helium atoms. As the final product and the helium atoms presumably also contain amounts of energy comparable with that of the emanation atom, the total energy in the atom must be exceedingly large.

**144 The range of the  $\alpha$ -particles and the period of decay.** A very interesting relation has been discovered by Geiger between the range of the  $\alpha$ -particles emitted by a radio-active substance and its coefficient of transformation. If the logarithm of the transformation constant is plotted against the logarithm of the range of the  $\alpha$ -particles emitted, the points for all the disintegration products of the uranium chain are found to lie on a single straight line. The shorter the transformation period the greater the range. Thus the more unstable the atom the greater the velocity of the  $\alpha$ -radiation. A similar relation holds for the members of the thorium series. The straight line in this case is parallel to that of the uranium chain but is displaced slightly, the  $\alpha$ -particles from the thorium series being ejected with rather higher velocities than those from products of similar period in the uranium chain.

This important result has not yet found an explanation. It suggests that the chance of an atom disintegrating increases

with the amount of energy which it can give out in forming the next member of the series. This seems not improbable on general grounds.

**145 Radio-activity of ordinary matter** The instances of radio-active change which we have considered naturally provoked the question as to whether all elements might not be radio-active to some extent. It was pointed out that every physical property as yet discovered in one element was possessed to a greater or smaller degree by all other elements. Magnetism, for example, provided an instance very much to the point. As tested by rough experiments only iron, cobalt, and nickel possessed magnetic properties to a noticeable degree. On making careful examination by powerful methods it was, however, found that all substances had some magnetic properties, being either para- or dia-magnetic.

The experiments were most conveniently carried out using an electroscope of the form shewn in Fig. 1. By lining the walls with sheets of the various substances under investigation, the amount of ionization produced in the presence of these different substances could be determined. It was found, as we have already mentioned, that there was always a certain amount of ionization in the gas of the electroscope, even in the absence of any recognized radio-active substance. The amount of this ionization was found to depend on the nature of the lining. This suggested that the source of the ionization was some form of radiation proceeding from the lining of the vessel. Campbell, after an exhaustive series of experiments, came to the conclusion that all substances shewed feeble radio-active properties, emitting rays which were characteristic of the metal.

The matter is an exceedingly difficult one to elucidate. Radium in very minute quantities is exceedingly widely distributed. Most soils contain an appreciable quantity, and most natural waters can be shewn to be feebly radio-active from the dissolved salts of radium which they contain. As radium emanation is a gas at ordinary temperatures it is always present in the air, in amounts which can be measured by suitable means, and which vary from day to day in a somewhat inexplicable manner.

The gas in the vessel is thus subjected to the ionizing influence of the  $\gamma$ -rays from the radium in the soil and its disintegration products in the atmosphere. This can be partly screened off by the use of lead blocks of considerable thickness. By finding how the ionization in the vessel decreases with the thickness of the screen, the residual ionization not due to these radiations can be calculated. A much better plan has been used by McClellan, who found that the waters of Lake Ontario were sufficiently deep to cut off the whole of the  $\gamma$ -radiation from the earth below them, while they themselves did not contain sufficient radio-active matter to cause any appreciable ionization in the electroscope. By making experiments over the lake he found that the number of ions formed per second per cubic centimetre of gas was reduced to 4.8 when the electroscope was of aluminium and 6.3 when it was of brass. The difference in the two values suggests that the small residual effect is due to the metal of the electroscope.

The effect is however so minute that it is difficult to decide with certainty. A single  $\alpha$ -particle from radium produces more than  $10^5$  ions during its path of 3 cms. The passage of a single  $\alpha$ -particle through each cubic centimetre of the gas, once every three hours, would therefore be sufficient to produce the average ionization found under these circumstances. The quantity of radio-active impurity in the metal necessary to produce an emission of this order is so minute that it is difficult to prove conclusively that the effect is not due to this cause, and Rutherford after a careful survey of the results has come to the conclusion that ordinary matter is not radio-active. On the other hand experimenters who have actually worked on the subject generally incline to the view that there is a residual effect due to the actual radio-activity of the elements themselves.

The survey of the subject has, however, led to the discovery of one more radio-active substance, namely potassium, which is found to emit  $\beta$ -radiation of very much the same type as that from uranium. The activity of a surface of potassium salt is quite appreciable, being in general about one per cent. of that of a surface of a salt of uranium. Rubidium has also been found to possess a similar radio-activity. In neither case is anything yet known as to the nature of the product, or the period of the change.

## CHAPTER XVI

### THE ELECTRON THEORY OF MATTER

146 The constitution of the atom The researches chronicled in the preceding chapters have thrown considerable light on the obscure subject of the nature of matter and the constitution of the atom. Let us recapitulate, briefly, the information which has actually been obtained on this important subject.

In the first case we have seen that matter of all kinds is capable of emitting electrons when subjected to suitable ionizing agents. Thus electrons are emitted from all kinds of matter under the influence of X-rays, or of ultra-violet light of suitable wave length. They are produced by the impact of the  $\alpha$ - and  $\beta$ -rays from radio-active substances, or by that of the charged gaseous ions. They are present in large numbers in the discharge tube, and may be produced from any metal, merely by raising its temperature to a sufficiently high value. They are, therefore, present in all kinds of matter, and thus presumably form an integral part of the atom of every element.

We have seen that the electrons emitted from different substances and by different ionizing agents are identical, except in velocity. Each electron carries a negative charge of  $4.77 \times 10^{-10}$  e.s.u., has a radius of the order of  $10^{-13}$  cm. (assuming it to be spherical) and a mass of about  $9 \times 10^{-28}$  gm. Further, the mass of the electron has been shewn (§ 111) to be probably due to the charge upon it. The mass of the electron is an insignificant part of the mass of the whole atom (about 1/1800 in the case of hydrogen) and its volume an infinitesimal fraction of the volume of the atom.

Since the atom as a whole is neutral (except when ionized by the emission of an electron) it must contain a positive charge

of magnitude  $Ne$ , where  $e$  is the electronic charge and  $N$  is the number of electrons in the atom

The fact that the  $\alpha$ -particles, which as we have seen are atoms of helium, are able to penetrate appreciable thicknesses of solid material effectively disposes of the hard or "solid" atom theory. It is evident that these results can only be explained on the assumption that the atoms are capable of inter-penetration to a very considerable extent. The modern view is that the atom consists merely of electrons and positive electricity. While this may not be definitely established we may affirm that none of our experiments have given any indication of the presence of anything besides.

Assuming, then, that an atom consists of electrons together with a corresponding positive charge it is easy to shew that the latter must occupy a space of very small dimensions. The experiments on the projection of hydrogen atoms by the impact of  $\alpha$ -particles (§ 107) shew that the former is projected with a velocity about 1.6 times that of the  $\alpha$ -particle. Assuming that the force is due to the mutual repulsion of the positive charges on the two particles it can be shewn that the centres of the two charges must approach to within  $3 \times 10^{-13}$  cm. and that they behave as point charges almost up to this distance. In other words the positive charge on the hydrogen atom is confined to a nucleus the radius of which is certainly less than  $10^{-13}$  cm., that is, less than that of the negative electron.

The positive charge is never found associated with a mass less than that of an atom. Thus the  $\alpha$ -particles are atoms of helium carrying a charge  $2e$ , while all the positive particles in a discharge tube (§ 55) have masses equal to those of the atoms and molecules in the tube. In no case has a positive charge been found associated with any particle of smaller mass than the hydrogen atom. As the negative electrons form but an insignificant fraction of the mass of the atom it is clear that this mass must be associated with the positive charge, and so far all experiments have failed to obtain the positive charge dissociated from this mass. It seems a reasonable inference that mass is a property of the positive charge.

Admitting then that the positive charge and the mass of the



atom is concentrated on a central nucleus of small dimensions, as suggested by Rutherford, the charge  $Ne$  on the nucleus can be calculated from observations on the scattering of  $\alpha$ -particles by the substance. The recent experiments of Chadwick on the subject (§ 107) may be taken as proving that  $N$  is equal to the atomic number of the element to an accuracy of at least 1 per cent. This confirms the suggestion, first made by van der Broek, that the number of electrons in the atom is equal to the atomic number of the element. Experiments on the scattering of X-rays (§ 87) and on the scattering of  $\beta$ -rays (§ 114) afford additional support to this conclusion, which may now be regarded as definitely established. The hydrogen atom, therefore, consists of a nucleus bearing a single positive charge, with one attendant negative electron.

We have seen that a particle carrying a charge  $e$  has an electromagnetic mass due to its charge and equal to  $\frac{2}{3} \frac{e^2}{a}$  where  $a$  is the radius. This result has been confirmed in the case of the negative electrons. It is clear from the formula that the electromagnetic mass is inversely proportional to the radius of the particle on which the electricity is concentrated. Thus if the positive nucleus carries the same charge,  $e$ , as an electron, its mass will be equal to that of a hydrogen atom if we assume it to be concentrated on a sphere of radius  $1/1800$  of that of the electron. The fact that the radius of the positive nucleus of hydrogen is at any rate less than that of an electron, certainly lends weight to the assumption. It would seem probable, therefore, that all mass is electromagnetic, and that the nucleus of the hydrogen atom is the *positive electron*, for which such continual search has been made. Rutherford has proposed to call this particle a *proton*.

**147. Constitution of atomic nuclei.** Admitting that the hydrogen nucleus is the unit of positive electricity, the composition of the nuclei of other elements can be deduced with some certainty. Helium, the second element in the series, has an atomic number 2, and, therefore, has a resultant positive charge equal to twice that carried by the hydrogen nucleus.

The mass of the helium atom is, however, very nearly four times that of the hydrogen atom, so that, unless we are to assume that a further concentration of the positive electricity takes place, four hydrogen nuclei will be required to produce the necessary mass. The simplest hypothesis we can make is to assume that the helium nucleus consists of a group of four hydrogen nuclei, or four positive electrons as we may call them, together with two negative electrons, thus producing a resultant mass of four and a resultant charge of two. The dimensions of the  $\alpha$ -particle as deduced from scattering experiments support this hypothesis.

The presence of negative electrons in the nucleus itself seems to be required by the phenomena of radio-activity. The  $\beta$ -rays are ejected from radio-active substances with enormous velocities, approaching in some cases within 1 per cent. of that of light, and these velocities could hardly be produced by the comparatively weak electric forces between the nucleus and its external electrons. They might, however, easily be produced by the very intense fields which must exist when a comparatively large number of charges are concentrated within a volume as small as that of an atomic nucleus. The energy of the  $\alpha$ -particles is probably due to the same cause. Ellis's experiments on characteristic  $\gamma$ -rays revealing the existence of electronic levels in the nucleus are strong additional evidence on the point.

The existence of isotopes (§§ 58, 139), that is to say, of atoms of identical, or nearly identical, chemical and physical properties but of differing mass, also points to the composite character of the nucleus. The chemical and physical properties of an element are undoubtedly determined by the number and arrangement of the external electrons in the atom. The mass of the atom depends only on the nucleus, on our assumptions, on the number of hydrogen nuclei contained in it. It should be possible, therefore, to build up atoms having the same nuclear charge, and thus the same atomic number, but differing in mass. Thus a nucleus made up of three hydrogen nuclei and one negative electron, would have a resulting charge and hence an atomic number of two. It would require two external electrons for its neutralization, and would thus exhibit the properties of helium, except that its mass would be three instead of four. In other

words it would be an isotope of helium. It is possible that this is the substance discovered by Sir J. J. Thomson in his positive ray photographs, and there is some evidence of the production of such atoms by the collision of  $\alpha$ -particles with other gases. Since every nucleus is made up of an integral number of hydrogen nuclei, the masses of the different nuclei must be capable of being represented by a series of whole numbers. This is in agreement with the observations of Aston. The fact that the atomic weight of hydrogen is rather greater than unity, if integral numbers are assigned for the masses of the other atoms, is probably due to the fact that there is a loss of energy when the hydrogen nuclei are combined to form a complex nucleus. Thus, on Einstein's theory, would automatically involve a corresponding loss of mass.

The significance of Soddy's rules for determining the chemical behaviour of the radio-active substances (§ 139) at once becomes apparent. As the nuclear charge is equal to the atomic number of the element an increase of unity in the nuclear charge obviously moves the element one space forward, that is, one space to the right in the periodic table of the elements. Thus the emission of a single  $\beta$ -particle from the nucleus, which will obviously raise the resultant positive charge of the nucleus by unity, will move the element one space to the right, as suggested by Soddy. Conversely the emission of an  $\alpha$ -particle which carries away two positive "atomic" charges with it, will decrease the positive nuclear charge by two, and will thus move the new element to a position two spaces to the left in the periodic table. All the elements occupying the same space in the table will possess the same nuclear charge and hence the same atomic number. The number and arrangement of their external electrons will therefore be identical, and thus they will have the same chemical properties. The atomic weight, and the mode of disintegration depend on the structure of the nucleus itself, and hence may be different for different isotopes. Owing to differences in the internal arrangement of the nucleus elements may even possess the same atomic weight, and still disintegrate in different ways. Such cases actually occur, for example, radium D and actinium B. These substances are not merely isotopic,

but also have the same atomic weight. The radio-active constants, and the products to which they give rise are, however, different for the two substances.

The actual structure of the nucleus is still obscure. The fact that the  $\alpha$ -particles emitted during radio-active changes consist of helium, would suggest that the helium nucleus is such forms a part of the structure of the heavier nuclei (see § 107).

This is also supported by Rutherford's experiments on the disintegration of atomic nuclei. The long range hydrogen particles are only ejected from nuclei whose atomic mass is represented by  $4n + p$ , where  $n$  is an integer, and  $p$  is not greater than 3. These results strongly suggest that when four protons are added to a nucleus they condense to form an  $\alpha$ -particle. From the comparative ease with which they are ejected it would seem that the additional protons over and above the number which can be combined into groups of four are less firmly attached to the main structure and revolve as satellites around it. This is the suggestion made by Rutherford.

The chief fact which has so far emerged as to the structure of the main mass of the nucleus is that of the existence of definite electronic energy levels within it, and the validity of the quantum relation for interchanges between those levels (§ 122). Our knowledge is not sufficient, however, to enable us to assert that these levels take the same form, or arise from the same causes, as the energy levels outside the nucleus.

The radius of the nucleus can be deduced from accurate experiments on the scattering of the  $\alpha$ -particles. Chadwick's experiments indicate that for the heavier elements the nucleus has a radius less than  $10^{-12}$  cm.

**148 Arrangement of electrons in an atom. The Thomson atom.** If we accept these conclusions, the atom of an element of low atomic weight is a comparatively simple structure. Thus the hydrogen atom would consist of a single positive nucleus, and one electron, the helium atom would have a nucleus bearing a double positive charge, with two electrons, and so on, each element differing from the one preceding it, in containing one additional charge on its nucleus, and one additional external

electron. It would seem at first sight that the arrangement and, therefore, the properties of these systems should be easily calculable. This, however, is far from being the case. Numerous mathematical physicists have attacked the problem, including Sir J. J. Thomson, Schott, Nicholson, and Bohr.

The earliest solution of the problem of electron grouping was obtained by Sir J. J. Thomson on the assumptions that the positive electricity is uniformly distributed throughout a sphere of atomic radius, and further that the rings of electrons are confined to a single plane. Neither assumption is valid, and the actual numbers have, therefore, no special significance. They will, however, serve well to illustrate the nature and effect of the laws of electron grouping and are, moreover, of considerable historic interest.

For any number of electrons up to five, it was found that they could arrange themselves in a single ring. A ring of six electrons was, however, unstable, and broke up into an outer ring of five, with a single electron in the middle. The ring of six could, however, be made stable by placing a single electron within it, and rings of seven and eight were also stable under the same conditions. An outer ring of nine, however, required three electrons to make it stable, and an outer ring of 16 no less than twenty. For large values of the number  $n$  in the outer ring the number  $p$  required inside it to ensure stability varies approximately as  $n^2$ . These inner electrons will arrange themselves according to the same laws as the others and will thus break up into a series of ring systems as indicated in Table XIII.

The results are very suggestive. In the first place it will be noted that a given grouping of electrons recurs again and again in the table. Thus the grouping 11, 5, 1, which commences series C, recurs again at the beginning of D with an extra ring of 15, and at the beginning of E with a further additional ring of 17. We should expect that systems with the same internal structure would exhibit very similar properties. If this is the case we should also expect that these systems should be separated by others having increasingly divergent properties. This is exactly what is found when the actual elements are arranged in order of their ascending atomic weights, elements



charges must be able to approach to within a distance much less than the radius of the atom, in fact they must act like single point charges until their distance apart is of the order of one ten thousandth of the radius of the atom. The maximum force exerted by a sphere of electricity would be at its surface, and quite insufficient in magnitude to produce the observed deflections.

**149 The Rutherford-Bohr atom** These considerations led Rutherford to put forward his nuclear atom, which has been already considered in part. The obvious objections to the nuclear theory are that, according to the ordinary electromagnetic theory such an atom would be completely unstable, and further that if one stable configuration could be found there must be in addition an infinite number of other configurations which would also satisfy the conditions. Thus, if the electrons are at rest outside the nucleus they will be unstable, but stability can be obtained (as in the similar case of the solar system) by setting them into rotation with suitable velocities. In this case, however, there should be an infinite number of possible orbits, since the only condition to be satisfied on classical theory is that the centrifugal force,  $mv^2/r$ , shall be equal to the attractive force between the electron and the nucleus. Again, on classical theory, the revolving electrons, being constantly accelerated, should radiate continuously, so that their energy, and hence velocity, would be continuously decreasing. The model proposed seemed, therefore, to lack the two outstanding features of the actual atom, namely, stability and definiteness.

Sir J. J. Thomson has recently suggested that stability might be obtained if the law of force between two charges at atomic or less than atomic distances differed from that of the inverse square law, which holds in the case of larger distances. The experiments of Chadwick on  $\alpha$ -ray scattering seem to negative this suggestion at any rate for distances greater than  $10^{-12}$  cm. and for positive charges. The evidence for the inverse square law between negative charges is not so conclusive.

The solution of the difficulty as to the stability of the atom is clearly to be found along the lines of the quantum theory. We

have already seen that in many instances the electron does not radiate continuously, as demanded by the classical theory, but that it emits either a whole quantum of energy, or no energy at all. Assuming that these conditions hold within the atom the quantum theory indicates the possibility that the revolving electrons may not be radiating energy, in which case the stability of the nuclear atom would be assured.

It was left to Bohr to make the brilliant suggestion that the second difficulty, the indefiniteness of the atom according to ordinary mechanical principles, might also be eliminated by an extension of the quantum theory. He suggested that a given orbit around the nucleus would only be stable, or "stationary" as he called it, if the energy of the electron in the orbit was related to the frequency of revolution in the orbit by a quantum relationship. Only orbits for which this relation was satisfied were to be regarded as stable or stationary, and only such orbits could have a permanent place in the atomic structure.

The exact form in which the quantum theory should be applied was not immediately apparent. Planck's constant,  $h$ , has the dimensions of energy  $\times$  time or momentum  $\times$  distance. The latter product is sometimes known as an "action." Bohr assumed that an orbit would be stationary if the electron rotating in it had an amount of "action" equal to an integral multiple of  $h$ , which may thus be regarded as the natural unit of action. For an electron describing a circular orbit we have, therefore,

$$mv \cdot 2\pi r = n\hbar, \quad (118)$$

where  $r$  is the radius of the orbit, and  $n$  is an integer. This may be expressed in the more general form

$$2\pi mr^2\omega = n\hbar, \quad (119)$$

where  $\omega$  is the angular velocity of the electron.

A stationary orbit must satisfy this relation, in addition to those required by ordinary mechanics. Thus only a select few of the orbits mechanically possible are possible electronic orbits.

**150. Bohr's theory of the hydrogen spectrum.** The fundamental truth of Bohr's assumptions was made evident by their startling success when applied to the case of the hydrogen atom. Since the hydrogen atom consists of a positive nucleus and



a negative electron, each of which behaves as a point charge, the calculation of the stationary orbits can be made with certainty and exactness.

Let  $e$ ,  $m$  be the charge and mass of the electron,  $Ne$  and  $M$  the charge and mass of the nucleus, and let  $r$  be the radius of the orbit in which the electron is moving with a velocity  $v$ . Equating the centrifugal force to the mutual attraction of the two charges we have as the mechanical condition of equilibrium

$$\frac{mv^2}{r} = \frac{Ne^2}{r^2}$$

If  $\tau$  is the time of revolution of the electron in its orbit  $v = 2\pi r/\tau$ , and, substituting this value of  $v$  in the previous equation,

$$\frac{4\pi^2 m r}{\tau^2} = \frac{Ne^2}{r^2} \quad (120)$$

Applying now Bohr's second postulate the "stationary" orbits are to be distinguished by the relation

$$2\pi m v^2 r = nh,$$

or, since

$$\omega = \frac{2\pi}{\tau},$$

$$\tau = \frac{4\pi^2 m r^2}{nh} \quad (121)$$

Substituting this value in (120) we have

$$r = \frac{n^2 \hbar^2}{4\pi^2 m N e^2}, \quad \dots \quad (122)$$

which gives the radii of the possible stationary orbits. All the quantities on the right-hand side of the equation are known. For the hydrogen atom, for which  $N=1$ , the radius of the smallest orbit, obtained by putting  $n=1$ , is  $0.52 \times 10^{-8}$  cm. The radii are proportional to the squares of the natural numbers, and all the orbits except the first are outside the generally accepted value for the radius of the hydrogen atom.

The kinetic energy of the electron in its orbit is  $\frac{1}{2}mv^2$  or  $Ne^2/2r$ . As the force between the electron and the nucleus is attractive the maximum potential energy will be when the electron is at an infinite distance from the nucleus. If  $W_\infty$  is this maximum value, the actual potential energy at a distance  $r$  from the nucleus is  $W_\infty - e \frac{Ne}{r}$ .

The total energy in the orbit is thus

$$\begin{aligned} W &= \frac{N e^2}{2l} + W_{\infty} = \frac{N e^2}{l} \\ &= W_{\infty} - \frac{N e^2}{2l} \\ &= W_{\infty} - \frac{2\pi^2 m N^2 e^4}{n^2 \hbar^2} \end{aligned} \quad (123)$$

substituting for  $r$  from (122)

Now by the ordinary quantum relation if an electron falls from an orbit of energy  $W_{n_1}$  to one of energy  $W_l$ , the difference is emitted as a monochromatic radiation of frequency  $\nu$  given by

$$\begin{aligned} \nu &= \frac{W_{n_1} - W_l}{h} \\ &= \frac{2\pi^2 m N^2 e^4}{h^3} \left\{ \frac{1}{n^2} - \frac{1}{n_1^2} \right\} \end{aligned} \quad (124)$$

substituting for  $W_{n_1}$  and  $W_l$  from (123). For hydrogen  $N = 1$ . Thus the lines in the spectrum of the hydrogen atom should be obtainable by substituting different integral values for  $n$  and  $n_1$  in this equation.  $n$  is the number of the orbit into which the electron falls,  $n_1$  that of the orbit from which it starts.

We have assumed, in the analysis, that the orbits are circular, that is to say that the mass of the electron is negligible in comparison with that of the nucleus. The necessary correction, which is easily made, gives for the hydrogen spectrum

$$\nu = 2\pi^2 \frac{Mm}{M+m} \frac{e^4 N^2}{\hbar^3} \left\{ \frac{1}{n^2} - \frac{1}{n_1^2} \right\} \quad (125)$$

If we put  $N = 1$ ,  $n = 2$ , we have

$$\nu = 2\pi^2 \frac{Mm}{M+m} \frac{e^4}{\hbar^3} \left\{ \frac{1}{4} - \frac{1}{n_1^2} \right\}, \quad (126)$$

which is of the form of the well-known Balmer's hydrogen series. The relation, however, is more than formal. The right-hand side of the equation consists only of quantities which are known to an accuracy of approximately 1 in 500. The value of the constant outside the bracket is known, from spectroscopic observations, to an accuracy of at least one part in 2,000,000. Any discrepancy would be fatal to the theory. The agreement is, however, exact to within the limits within which the various quantities are known.

It is customary, in spectroscopy, to use instead of the frequency  $\nu$  a quantity  $\nu' = \frac{1}{\lambda} = \frac{\nu}{c}$ , where  $c$  is the velocity of light. The Balmer's series is thus given by  $\nu' = R \left( \frac{1}{2^2} - \frac{1}{n_1^2} \right)$ , where  $R$  is known as Rydberg's constant and has the value  $1.09677 \times 10^5$ . The corresponding factor in (126) on evaluation gives  $1.0955 \times 10^5$ . The agreement is thus perfect, within the limits of experimental error.

Other series indicated by (125) are also known. Putting  $n = 1$ , we have a series in the ultra-violet discovered by Lyman, if we

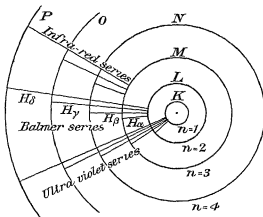


Fig 107

make  $n = 3$ , we have a series in the infra-red discovered by Paschen. These hydrogen series are indicated diagrammatically in Fig 107.

Another system which lends itself to exact calculation is that of the helium atom which has already lost one electron. The spectrum of the ionized helium atom should be represented by (125) by making  $N = 2$ , the atomic number of helium. The series spectra for this atom should, therefore, be represented very nearly by the relation

$$\nu' = 4R \left( \frac{1}{n^2} - \frac{1}{n_1^2} \right)$$

Series of this form have been known for some time, having been

discovered by Pickering, and by Fowler. They were formerly attributed to hydrogen. Bohr's formula, however, indicates that the value of the Rydberg constant should be slightly greater for helium than for hydrogen, since the mass,  $M$ , of the nucleus is greater. The spectroscopic data give  $R$  from the acknowledged hydrogen series as 109677.691 and from the Fowler-Pickering series as 109722.111. This small difference between the two constants can be used, in conjunction with (125), to calculate the ratio of the mass of an electron to the mass of the hydrogen nucleus, assuming the known value for the atomic weight of helium. Combining this with the electro-chemical equivalent of hydrogen we obtain for  $e/m$  the value  $1.769 \times 10^7$  in e.m.u. agreeing with the best direct determinations. For the systems to which Bohr's theory can be rigorously applied it is thus amply justified by the results.

**151. The normal hydrogen atom.** Since the hydrogen atom possesses only one electron only one of the many stationary orbits can actually be occupied at one time. In the normal condition of the atom this will be the innermost one, since this is the position of minimum energy. The remaining orbits are potential orbits only. This is borne out by the dispersion of hydrogen, which is explicable on the assumption that hydrogen possesses normally only a single absorption band in the ultra-violet.

It also explains the rather puzzling fact that hydrogen does not absorb selectively radiation corresponding to its own emission spectrum. Any system should shew selective absorption for radiation corresponding in frequency to its own natural frequencies, and the effect is very well shewn by the Fraunhofer lines in the solar spectrum, and the well-known reversal of the sodium lines on passing through sodium vapour.

In the case of hydrogen, the orbits giving rise to the main lines in the spectrum are not occupied normally, and hence no selective absorption is to be expected. When, however, the gas is ionized, then the electron on its return may occupy successively one or more of these orbits before its final return to the most stable of all. Thus it is only when the substance is ionized

that light is emitted. We might expect that selective absorption would occur when light is passed through the ionized gas, and it is interesting to note that Ladenburg obtained evidence of selective absorption of the hydrogen lines in the Balmer series by passing the light from a very bright discharge in hydrogen through a long tube containing hydrogen which was kept feebly glowing by a much weaker discharge.

It may also be noted that a single atom at a given instant only emits a single line of the whole spectrum. An explanation of these phenomena on the lines indicated was given by Sir J. J. Thomson, prior to the complete theory of Bohr.

Assuming the electron to occupy the innermost orbit we should be able to calculate the ionization potential and the various resonance potentials (§ 32) of the atom. The ionization potential is the work which must be done to remove an electron from the innermost orbit to infinity, and should therefore be given by  $Ne/2$ . This corresponds to 13.7 volts. This value is distinctly less than that obtained by direct experiment (§ 31).

The direct experiments, however, are made not with hydrogen atoms but with hydrogen molecules, and the effect of the nucleus of the second atom in the molecule cannot be ignored. We may assume that the molecule is first dissociated by electronic impact and then ionized. The dissociation voltage of the hydrogen molecule cannot be calculated, since its structure has not yet been satisfactorily determined. From direct experiments the dissociation potential has been estimated by Langmuir at about 3.5 volts. The ionization potential of hydrogen should thus be  $13.7 + 3.5$  or 17.2 volts. This agrees sufficiently closely with the experimental value. It may be mentioned that many workers have recorded a "critical potential" for hydrogen at 13.4 volts. This is generally regarded as a resonance potential, but its value agrees closely with that calculated for the ionization potential of the hydrogen atom.

**152 Elliptic orbits** Sommerfeld's theory. It can be shown that the circular orbits described in the previous sections are not the only orbits which will satisfy the mechanical and quantum relations for a stationary orbit. The mechanical con-

ditions for stability under the action of a central force can be satisfied by a particle vibrating along a straight line passing through the centre of attraction, and if the particle possessed the appropriate energy the quantum conditions could also be satisfied. This type of motion is obviously not possible as an electronic orbit as it would carry the electron straight into the atomic nucleus. Hence for the innermost orbit, possessing only one quantum of action, or one quantum number as it is called, the circular orbit is the only possibility.

This, however, is not the case with orbits of higher quantum number. It is easy to shew that a particle describing an elliptical

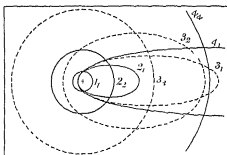


Fig. 108

orbit around the nucleus as focus will satisfy the mechanical conditions for stability. As the particle describes its ellipse its distance from the nucleus increases and decreases alternately. Its motion can thus be regarded as the sum of two motions, one along the radius, the other at right angles to this. The former is known as the radial, the latter as the azimuthal motion. Each of these motions must, separately, satisfy the quantum relation laid down by Bohr. Thus the total quantum number of the orbit may be divided between these two possible motions, and the eccentricity of the ellipse is determined by the mode of division.

It is customary to represent the mode of division by giving first the total quantum number, and secondly the azimuthal quantum number of the orbit. The radial quantum number is the difference between these figures. Thus if we consider the possible orbits for which  $n = 3$  (see § 149), we may represent them by the symbols  $3_3, 3_2, 3_1, 3_0$ . The  $3_3$  orbit has obviously a radial

quantum number of 0. There is thus no radial movement and the orbit is the circular orbit already discussed. The  $3_0$  orbit conversely corresponds to motion only along the radius, and is impossible since the path would pass through the nucleus. The remaining orbits  $3_2$  and  $3_1$  represent ellipses of increasing radial movement and hence of increasing eccentricity. These orbits, together with those for  $n = 2$ , are shown in Fig. 108.

Sommerfeld has shown that the elliptical orbits possess the same "action" as the circular orbits of the same quantum number, and are, in fact, experimentally indistinguishable from them so long as the atom is not subjected to any external field of force. Thus Bohr's calculation of the hydrogen spectrum is not affected in any way by the possibility that some of the orbits described may be elliptical and not circular, as assumed. On the other hand, the two kinds of orbits give rise to different effects if the atom is subjected either to a magnetic, or an electric field, and in this way Sommerfeld has been able to account for both the Zeeman and the Stark effects (§ 158).

In the previous analysis it is assumed that the mass of the electron remains constant. This, however, is not exactly true, since the mass varies with the velocity. Hence the electron in an elliptic orbit has a rather greater mass when it is close to the nucleus than in the more distant portions of its path. As a result the orbit is not exactly an ellipse, and the particle does not exactly retrace its path. The orbit, in fact, is actually an unclosed curve, but may be regarded as an ellipse of which the major axis rotates about the nucleus. This has been used by Sommerfeld to explain the detailed structure shown by spectral lines, under high dispersion.

**153. The electronic structure of the atom.** The principles enunciated by Bohr can only be applied rigorously to the hydrogen atom and the ionized helium atom. As soon as a second electron is added to the structure the problem becomes mechanically identical with that of three gravitating bodies, which is still unsolved. Thus no model which satisfies all the experimental data has been evolved even for such comparatively simple systems as the hydrogen molecule, and the neutral helium atom. The

most probable suggestion for the latter is that the two electrons each describe a  $1_1$  circular orbit, the planes of the two orbits being inclined obliquely to each other at an angle of  $120^\circ$  (Fig. 109). This model accounts satisfactorily for the optical spectra of helium but does not give the correct ionization potential.

The calculation of the orbits for the more complex atoms of higher atomic number obviously presents formidable difficulties and uncertainties. The most successful attempt to solve the problem is that of Bohr. He starts from the observation that the loss of an electron during ionization apparently leaves the orbits of the other electrons unaltered. This is supported by the fact that the energy of the  $L$  level in an atom as calculated from

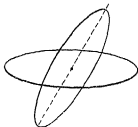


FIG. 109

the X-ray emission spectra agrees with the value calculated from absorption data (§ 95). In the former case the  $K$  level has lost an electron, in the latter it has its full complement, but the energy of the  $L$  level remains the same. He assumes then that the addition of further electrons will not change the nature of the orbits already occupied in the atom (they will, of course, shrink owing to the increased nuclear attraction), and attempts to calculate, partly from energy considerations and partly from optical data, which orbit of those theoretically possible the extra electron will occupy. The calculations are obviously laborious and complex, and have not yet been published in detail.

Bohr's latest scheme is indicated, in part, in Table XIV. The numbers in the vertical columns indicate the number of electrons describing an orbit of the type indicated (by its quantum numbers) at the head of the column. Thus beryllium is assigned two electrons describing circular  $1_1$  orbits, the orbits being pre-



sumably crossed as suggested for the helium atom, and two electrons describing elliptical  $2_1$  orbits

TABLE XIV

	$K$ $1_1$	$L$ $2_1, 2_2$	$M$ $3_1, 3_2, 3_3$	$N$ $4_1, 4_2, 4_3, 4_4$	$O$ $5_1, 5_2, 5_3$	$P$ $6_1, 6_2$	
1 H	1						
2 He	2						
3 Li	2	1					1st short series
4 Be	2	2					
5 B	2	2, 1					
6 C	2	2, 2					
10 Ne	2	4, 4					
11 Na	2	4, 4	1				2nd short series
12 Mg	2	4, 4	2				
13 Al	2	4, 4	2, 1				
18 A	2	4, 4	4, 4				
19 K	2	4, 4	4, 4	1			1st long series
20 Ca	2	4, 4	4, 4	2			
21 Sc	2	4, 4	4, 4, 1	2			
22 Ti	2	4, 4	4, 4, 2	2			
29 Cu	2	4, 4	6, 6, 6	1			
30 Zn	2	4, 4	6, 6, 6	2			2nd long series
31 Ga	2	4, 4	6, 6, 6	2, 1			
36 Kr	2	4, 4	6, 6, 6	4, 4			
37 Rb	2	4, 4	6, 6, 6	4, 4	1		
54 X	2	4, 4	6, 6, 6	6, 6, 6	4, 4		
55 Cs	2	4, 4	6, 6, 6	6, 6, 6	4, 4	1	Series containing rare earth metals
56 Ba	2	4, 4	6, 6, 6	6, 6, 6	4, 4	2	
57 La	2	4, 4	6, 6, 6	6, 6, 6	4, 4, 1	2	
79 Au	2	4, 4	6, 6, 6	8, 8, 8, 8	6, 6, 6	1	
86 Em	2	4, 4	6, 6, 6	8, 8, 8, 8	6, 6, 6	4, 4	

154 Electron grouping and the periodic classification of the elements In one important aspect the scheme outlined in Table XIV resembles Thomson's earlier solution of the problem It indicates that the total number of electrons which can occupy

a given energy level is limited. Thus the *K* level can contain only two electrons, the *L* level only eight, and so on, and as in the earlier theory the level when containing its full complement of electrons forms a very stable structure. In fact the completion of a given level always corresponds with the appearance of one of the inert gases, helium in the case of the *K* level, and neon in that of the *L* level. The element of next higher number must, therefore, contain a single electron in a higher level, and according to Bohr this occupies the most eccentric of the orbits open to it in this new level. Its course carries it far beyond the limits of the structure of the rest of the atom (Fig. 108). If we consider the sodium atom, for example, the two electrons in the *K* level and the eight in the *L* level will form a comparatively close tangle around the central nucleus. At external points therefore, the system will act almost like a point charge, the magnitude of the charge being the difference between the nuclear charge (11), and the electronic charges (10). The inner electrons practically screen the  $3_1$  electron from the nuclear attraction when it is in distant parts of its track, and the attraction is, therefore, only slight. In other words the sodium atom would easily lose the  $3_1$  electron, and acts as an electro-positive element. An exactly similar state of affairs is obviously reached after each element of the helium group.

Magnesium, with two electrons in  $3_2$  orbits, can clearly lose both of them. On the other hand, the screening effect is slightly less efficient, owing to the increase of one unit in the nuclear charge, and the element is divalent but rather less electro-positive than sodium. These groupings recur from point to point in the table, or in other words the properties of the different atoms will be a periodic function of their atomic number.

Bohr's scheme, has, however, the merit of accounting for the actual scheme of the periodic table with an accuracy to which the earlier theories could lay no claim. Coming down the table we find that argon is assigned eight electrons in the *M* level, and it must be assumed that this number produces a quasi-saturation of this level, for Bohr's calculations show that the next electron is bound, not in an *M* orbit, but in an eccentric orbit in the *N* level. Potassium has thus all the properties of

an alkali metal, and calcium of an alkali earth. Further calculation shews, however, that with the next atom, scandium, the most stable orbit for the new electron, owing to the increase in the nuclear charge, is not an  $N$  orbit, but one of the circular orbits of the  $M$  level, hitherto unoccupied. Scandium has thus only two electrons in  $N$  orbits, and its electronic structure is radically different from that of aluminium. We have, in fact, reached the beginning of the first of the long periods in the periodic table. The eight electrons which saturate the  $M$  level for a nuclear charge of 20 or less, no longer do so when the nuclear charge is increased beyond this, and for nuclear charges of 29 and over the  $M$  level contains eighteen electrons.

The process is repeated twice in the  $N$  level. Thus krypton has eight electrons in this level, the next most stable orbit being in the  $O$  level. The filling up of ten vacant places in the  $N$  level gives rise to the second long period, the structures of corresponding elements in the two long series being similar. With xenon the  $N$  levels contain eighteen electrons, and the  $O$  level eight, both being temporarily saturated. Each, however, is capable, with nuclei of higher charge, of accommodating further electrons, and the filling up of these vacant inner orbits, leaving the outermost structure almost unaltered, gives rise to the rare earth series, which hitherto it has not been possible to fit into any orderly scheme.

A close study of Table XIV will no doubt suggest further relations between the Bohr scheme and Mendeleef's classification. The fact that a table of electron grouping, drawn up from a few fundamental principles with the aid of purely optical data, should agree so closely with a table drawn up purely from chemical considerations provides strong evidence that, although modifications of detail may be necessary, Bohr's method of analysis and fundamental principles are sound.

**155. Electron theory of valency, and chemical combination.** The class of chemical compounds in which the component atoms are each electrically charged is readily accounted for on the principles of electron grouping. We have already pointed out that the last electron in the atom of an alkali metal is very

loosely attached to its nucleus at the most distant part of its orbit, and is therefore not unlikely to be captured by some other nucleus. We may assume, with Sir J. J. Thomson, that an atom in which the number of electrons in its outer level is only slightly less than that required for saturation has a strong tendency to bind an electron in one of its vacant orbits. In short, the electronic structure has a tendency to revert to that of the nearest inert gas. Thus in the typically polar compound, potassium chloride each atom has the electronic structure of argon, but the potassium nucleus has a resultant positive charge of two units more than the chlorine nucleus. Each atomic system thus remains distinct and separate, and in the structural sense there is no "molecule" of potassium chloride.

Thus, perhaps startling, conclusion is amply supported by experiment. In the solid state the X-ray analysis of the crystals shows that each potassium atom is equally related to each of the surrounding eight chlorine atoms (§ 92), and each chlorine atom is similarly related to eight atoms of potassium. In solution the theory of electrolytic dissociation has long taught that the two atoms behave as independent entities. These principles enable us to give an adequate account of the valencies exercised in the polar type of compound.

Sir J. J. Thomson has, however, drawn attention to a second class of chemical compounds in which the component atoms are certainly not electrically charged, that is to say in which there has been no transference of an electron from one atom to the other. The absence of charge on the atoms of such compounds can be demonstrated by their behaviour in the positive ray tube. In the case of the polar compounds the atoms, on dissociation by the discharge, are found to carry positive or negative charges. In the case of the non-polar compounds, of which we can take the hydrogen or oxygen molecule as typical, the individual atoms are not charged on dissociation, and are presumably therefore also uncharged in the molecule. For these compounds we know from the gas laws that the molecule acts as a single entity.

Langmuir, from purely chemical considerations, has proposed a static atom in which the electrons occupy the corners of a cube, and has assumed that the system will be saturated if all

eight corners are occupied. In the oxygen atom, with atomic number 8, subtracting the two  $K$  electrons, we have six electrons for the eight possible places. If, now, a second oxygen atom is placed face to face with the first it is possible to arrange that every corner shall be occupied by an electron, the four electrons occupying the corners of the common face forming part of the structure of each atom (Fig 110 (a)).

The Langmuir atom has no physical basis, but it has been very successful in explaining many obscure phenomena of chemical combination. Its more valuable features will probably be translatable into the terms of Bohr's theory. In particular

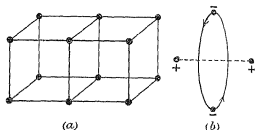


Fig 110

the idea of one pair of electrons being shared between two atoms can be adopted without difficulty by imagining that in the case of a non-polar compound two or more of the electrons, in the outer orbits, have their paths changed so that they describe new paths embracing both the atomic nuclei. There is nothing improbable in this supposition, but further analysis will be necessary before the possibility and the forms of these orbits can be demonstrated.

Bohr suggested, some years ago, that in the simplest of these compounds, the hydrogen molecule, the two electrons described a common circular orbit with its plane at right angles to the line joining the two nuclei (Fig 110 (b)). The model, however, did not give the correct ionization potential, and has been more or less abandoned.

**156. The theory of X-ray spectra.** It is now possible to discuss in rather more detail Bohr's theory of X-ray spectra, which has already been dealt with from its experimental aspects

in an earlier chapter (§ 98). The characteristic  $K$  radiation is emitted by electrons which fall back from various outer energy levels into the innermost ring. The electrons in the  $K$  ring come directly under the influence of the nucleus, and the effect of the electrons in the outer levels upon them is comparatively slight. The energy of the  $K$  orbit is, therefore, governed almost entirely by the nuclear charge. We can thus regard the  $K$  radiation as an example of the hydrogen type of spectrum, and, in fact, we must regard the Lyman hydrogen series as being the  $K$  radiation, and the Balmer series as the  $L$  radiation, of hydrogen.

The  $K$  radiation of an element should thus be represented by an equation of the type (125), where  $n$ , the quantum number of the arrival orbit, is put equal to 1. Thus for the  $K_\alpha$  line, due to the transference of an electron from the  $L$  to the  $K$  level, we should be able to write approximately

$$\nu' = RN^2 \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} R N^2$$

A correction must, however, be made in  $N$  to take into account the presence of the second electron present in the  $K$  level of all elements of higher atomic number than hydrogen. The negative charge on this electron will reduce the effective charge on the nucleus, so that we must substitute for  $N$  a quantity  $N - b$ , where  $b$  is a constant which cannot be greater than unity. We thus arrive at the relation for the  $K_\alpha$  line

$$\nu' = \frac{3}{4} R (N - b)^2,$$

which is of exactly the form of the empirical relation given by Moseley. Substituting its proper value for Rydberg's constant  $R$ , making  $N = 46$ , the atomic number of silver, and putting  $b = 1$  (approximately) we obtain as the calculated value for the wave length of the  $K_\alpha$  line of silver the value  $0.57 \times 10^{-8}$  cm which is in good agreement with the actual measurements.

The fact that the  $K_\alpha$  line is found to be a doublet is due, as Sommerfeld first pointed out, to the possibility of the  $L$  electron describing an elliptic as well as a circular orbit. If the mass of the electron was independent of its velocity the energies of the two orbits would be the same, and the frequency of the line emitted by an electron falling from either of these orbits into

the  $K$  orbit would be the same. The velocity of an electron in its orbit is, however, so great, particularly with elements of high atomic number, that the variation of mass with speed cannot be altogether ignored. In a circular orbit the speed is constant, but in the elliptic orbit the speed and the mass of the electron are increased as it approaches the nucleus. The energy in an elliptic orbit is, therefore, slightly less than that in a circular orbit, although the quantum number (which refers to "action" and not energy (§ 150)) is the same. We have thus two critical absorption frequencies  $L_1$  and  $L_2$  corresponding to the two kinds of  $L$  orbits, and two slightly different frequencies for the  $K_\alpha$  radiation corresponding to the energy difference ( $W_{L_1} - W_K$ ) and ( $W_{L_2} - W_K$ ). The energy difference ( $W_{L_1} - W_{L_2}$ ) has been calculated by Sommerfeld, and varies as the fourth power of the atomic number. The calculated frequency difference between the two  $K_\alpha$  components is in good numerical agreement with the observations. The origin of the third  $L$  absorption frequency is not accounted for on the theory.

**157 Orientation of the atom.** The "third" quantum number. So far we have been considering the atom as completely free from all external fields of force. In practice no atom is entirely uninfluenced by magnetic or electric fields although such fields may be infinitesimally small. Owing to the field of force the different planes through the nucleus in which the orbits of the electrons may lie are not identical. There is always a unique direction marked out in space, the direction of the resultant field, which could be identified by sufficiently sensitive appliances, and thus the space in which the atom lies is, to this extent, anisotropic.

A rigorous application of quantum mechanics demands that where a unique axis exists the movement in a plane perpendicular to this unique direction shall also be quantized, that is to say, equation (119) must apply to the resolved part of the motion in this plane. The Bohr orbits can, therefore, only lie in such a plane or planes in space as satisfy this third condition. If  $I$  is the "action" in the plane of the actual orbit of the electron, the "action"  $I_\perp$  in a plane perpendicular to the unique axis  $OZ$  will

be  $I \cos \alpha$ , where  $\alpha$  is the angle between the axis  $OZ$  and the normal to the plane of the orbit. The new postulate is that  $I_z = I \cos \alpha = n_1 \hbar \cos \alpha$  shall be an integral multiple of Planck's constant, i.e.

$$n_1 \cos \alpha = n_z \quad (127)$$

where  $n_z$  is an integer and is known as the third quantum number. For a one quantum orbit, where  $n_1 = 1$ , this can only be satisfied if the plane of the orbit is either parallel or perpendicular to the direction of the field. The atom must, therefore, be orientated in one of these two directions, no matter how weak the field may be.

With orbits of higher total quantum number the number of possible orientations increases. Thus if  $n = 2$ ,  $\alpha$  may have the values  $0^\circ$ ,  $60^\circ$ , or  $90^\circ$ . This orientation of the atom in the weakest fields, which is amply supported by recent experimental evidence, leads to very important results in magnetic theory.

**158. Emission of light. The Zeeman effect.** It is outside the purpose of this volume to deal with the application of Bohr's theory to the optical spectrum of the elements. Students may be referred to the works of Sommerfeld and N. R. Campbell mentioned in the references at the end of this chapter for full information on this point. Historically the first accurate proof that the vibrations constituting light were emitted by electrons was provided by the Zeeman effect.

If a source of light, say, for example, a sodium flame, be placed between the poles of a strong electromagnet, and the light emitted be analysed by a powerful interference spectrometer, it is found that the spectral lines emitted by the source are split up into two or more components. If the lines are observed in a direction at right angles to the magnetic field, the original line is seen to be accompanied by two other lines, one on each side of it, and separated from it, in the case of very strong fields, by a distance which may amount to as much as one-fifth of the distance separating the two sodium lines. If the light is viewed in a direction parallel to the lines of the field, the centre line disappears, and the two outer components are seen alone. This is known as the Zeeman effect. The two outer components are circularly polarized in opposite directions, when viewed along the lines of the field.



An explanation of the Zeeman effect has been given by Lorentz. Since the systems emitting the light are influenced by a magnetic field they must obviously be charged. Let  $e$  be the charge and  $m$  the mass of one of these vibrating systems. Assuming that the vibrations are simple harmonic they may be resolved into components perpendicular and parallel to the magnetic field. The vibrations parallel to the field will be unaffected by the field since a magnetic field has no effect on a charged particle moving parallel to the lines of force. The component at right angles to the field may be regarded for convenience as equivalent to two equal and opposite circular rotations, executed in the same period, but in opposite directions. In other words we may regard the particles as describing circular orbits of equal radius, and in equal times, but in opposite directions.

Let  $f$  be the restoring force in the absence of the field. Then since the motion is simple harmonic

$$f = kr,$$

where  $r$  is the radius and  $k$  a constant. Also by the ordinary mechanical laws

$$f = \frac{mv^2}{r}$$

If  $T$  is the time of vibration,  $v = \frac{2\pi r}{T}$ ,

$$k = \frac{4\pi^2 m}{T^2}$$

The field  $H$  produces a force on the particle equal to  $Hev$  which since it is at right angles to the field and to the direction of motion of the particle must always act along the radius. Since the two orbits are described in opposite directions it will in one case be directed outwards, in the other inwards, along the radius. The direction of the force depends on the direction of rotation and the sign of the charge and can be determined by the usual rule when these are known. Thus, when the field is applied we have

$$\left. \begin{aligned} \frac{mv_1^2}{r_1} &= kr_1 - Hev_1 \text{ for the clockwise rotation} \\ \frac{mv_2^2}{r_2} &= kr_2 + Hev_2 \text{ for the counter-clockwise rotation} \end{aligned} \right\}, \quad (128)$$

where  $e$  is supposed to carry its own sign. Substituting in these equations for  $k$  and for the velocities, we have

$$\frac{4\pi^2 m}{T_1^2} = \frac{4\pi^2 m}{T^2} - H e \frac{2\pi}{T_1},$$

$$\frac{4\pi^2 m}{T_2^2} = \frac{4\pi^2 m}{T^2} + H e \frac{2\pi}{T_2},$$

or on subtracting

$$\begin{aligned} 4\pi^2 m \left\{ \frac{1}{T_1^2} - \frac{1}{T_2^2} \right\} &= -2\pi H e \left\{ \frac{1}{T_1} + \frac{1}{T_2} \right\}, \\ \frac{e}{m} &= \frac{2\pi}{H} \frac{T_1 - T_2}{T_1 T_2} = \frac{2\pi}{H} \frac{T_1 - T_2}{T_0^2} \end{aligned} \quad (129)$$

writing  $T_0$  for  $T_1 T_2$  which is permissible since the change produced in the periods is very small. But if  $\lambda$  is the wave length of the light emitted  $\lambda = cT$  where  $c$  is the velocity of light. Hence finally if  $\lambda_0$  is the original wave length,  $\lambda_c$  that of the clockwise disturbance,  $\lambda_a$  that of the counter-clockwise rotation

$$\frac{e}{m} = \frac{2\pi c}{H} \frac{\lambda_c - \lambda_a}{\lambda_0^2}. \quad (130)$$

Thus if the particles carry a positive charge so that  $e$  is positive the component of greater wave length will be circularly polarized in a clockwise direction, if negative it will be polarized in a counter-clockwise direction, as viewed along the positive direction of the lines of the magnetic field. The latter is found experimentally to be the case. Hence the particles emitting the light are negatively charged.

The component of the vibration parallel to the field will produce no radiation in this direction, as a charged system gives no radiation along the line of its motion (§ 77). If viewed at right angles to the field this component will give a line in the undisplaced position of the original line which will be plane polarized, the direction of the electric displacement being parallel to the field. The two displaced lines will be plane polarized in a plane at right angles to this, since from this direction their orbits are viewed end on. These predictions are verified by experiments.

Runge and Paschen found that for a certain series of mercury

lines the value of  $\frac{\lambda_0 - \lambda_n}{\lambda_0^2}$  was  $-3.14$  for a magnetic field of 24,600 gauss. Substituting these values in the equation (130), we have

$$\frac{e}{m} = \frac{2.14 \times 2\pi \times (3 \times 10^{10})}{24,600} = 1.65 \times 10^7$$

This value agrees closely with the value of the same ratio for a negative electron. The systems emitting the lines in the spectra are, therefore, electrons.

The Lorentz theory ignores all the conditions imposed by quantum dynamics. The introduction of quantum considerations can be shown to leave the solution unchanged. Let us consider, for simplicity's sake, a single electron describing a one quantum orbit around the nucleus. The plane of the orbit must (§ 157) be either parallel or perpendicular to the magnetic field. The effect of a magnetic field on the electronic orbit can be determined by a well-known theorem due to Larmor. He has shown that the form of the orbit and the velocity with which it is described may be regarded as unaltered by the magnetic field if we refer all our quantities to a system of co-ordinates which rotates around the direction of the magnetic field with an angular velocity  $\omega$  given by

$$\omega = \frac{e}{m} \frac{H}{c},$$

where  $H$  is the magnetic field.

This velocity can be shown to be small compared with the velocity of the electron in its orbit. The orbit may thus be regarded as of constant shape and size but precessing slowly around the direction of the magnetic field. It can further be shown that, if the precession is slow the quantum conditions will be unaffected, and an  $n$  quantum orbit will remain an  $n$  quantum orbit in spite of the new precessional motion. This is known as the principle of *adiabatic invariance*. The kinetic energy of the electron in its orbit will, however, in general be slightly altered. Let us consider, for the sake of simplicity, a single electron describing a one quantum orbit about the nucleus. The plane of this orbit must be (§ 157) either parallel or perpendicular to the lines of the field. If parallel, the precession will not change the kinetic energy of the electron in its orbit. If, however, the orbit

is perpendicular to the lines of force the velocity of the electron is unchanged with respect to the *moving* axes of reference. If the axes move in the direction in which the electron is rotating in its orbit its actual velocity referred to a fixed axis is obviously increased. If the two rotations are opposed, it is diminished. Hence the energy of the electron in the orbit is either increased or decreased according to its direction of rotation by some amount  $\partial T$ . The frequency of the radiation emitted by an electron falling into the orbit from without the atom, will, by Bohr's principle, be decreased or increased by an amount given by

$$h \partial \nu = \pm \partial T$$

The single line will thus be split up into three components, as in the Lorentz theory.

It can be shown that

$$\partial T = n_z \frac{\omega}{2\pi} h,$$

where  $n_z$  is the third, or equatorial, quantum number in relation to the direction of the field (127). If we put  $n_z = 1$ , we have

$$h \partial \nu = \pm \frac{\omega}{2\pi} h$$

$$\partial \nu = \pm \frac{eH}{4\pi mc}$$

The frequency difference between the two lines is thus  $\frac{eH}{2\pi mc}$  which reduces to the Lorentz formula, on substituting wave lengths for frequencies. It will be noticed that Planck's constant has disappeared from the final relation.

A similar line of reasoning enables us to account for the decomposition of spectral lines by a strong electric field (the Stark effect). This effect is not explicable in the classical theory.

**159. Electron theory of metallic conduction.** The phenomenon of the conductivity of metals for electricity, at any rate as far as its main outlines are concerned, presents no difficulties on the electron theory. We have seen (§ 64) that a metal contains free electrons which are capable of moving about through it, and behave very much as the molecules of

an ordinary gas. The actual cause of emission of these electrons is perhaps not altogether clear, but all metals are electro-positive, that is to say, they are substances the atoms of which readily emit electrons. The atmosphere of electrons is in equilibrium with the atoms, and the number per unit volume is thus kept constant by a process analogous to that of evaporation. We may regard the pressure of the electrons in the metal as analogous to that of a saturated vapour in contact with its own liquid.

We have seen (§ 64) that these electrons partake of the energy of thermal agitation of the surrounding atoms, and may be treated by the ordinary principles of the kinetic theory of gases. The velocity  $v$  of thermal agitation is, therefore, given by

$$\frac{1}{2}mv^2 = \alpha\theta \quad . \quad . \quad . \quad (131)$$

where  $\alpha$  is a constant which is the same for all gases, and  $\theta$  is the absolute temperature. The velocity can thus be determined, for if  $m_h$  and  $v_h$  are the mass and velocity of the hydrogen molecule we have

$$\frac{1}{2}mv^2 = \alpha\theta = \frac{1}{2}m_h v_h^2,$$

$$\therefore \quad v^2 = \frac{m_h}{m} v_h^2.$$

But the velocity of a hydrogen molecule in a gas at  $0^\circ \text{C}$ . is  $1.842 \times 10^5 \text{ cm/sec}$ . Hence

$$v^2 = 2 \times 1840 (1.84 \times 10^5)^2,$$

$$v = 11 \times 10^6 \text{ cm per sec},$$

since the mass of an electron is about  $1/1840$  that of a hydrogen atom.

These velocities are equally distributed in all directions and thus cause no transference of electricity through the conductor. If, however, an electric field  $X$  is applied it will cause a steady drift of the electrons in the opposite direction to the field, since the electrons are negatively charged. The positive atoms being fixed do not move under the field and therefore add nothing to the current. Thus if  $n$  is the number of electrons per unit volume, the current across any cross section of the conductor of area  $A$  is given (5) by  $i = AnekX$

where  $k$  is the mobility of the electron. The mobility of the

electron can be calculated in exactly the same way as the mobility of a charged ion in a gas and is therefore (12) given by  $\frac{1}{2} \frac{e \lambda}{m v}$  or substituting for  $m$  from (131) by  $\frac{e \lambda v}{4 \alpha \theta}$ . Thus

$$i = A \frac{n e^2 \lambda}{2 m v} X = A \frac{n e^2 \lambda v}{4 \alpha \theta} X \quad (132)$$

If the field is uniform we have  $X = \frac{V}{d}$ , where  $d$  is the length of

the conductor and  $V$  the applied E.M.F. Thus  $i = \frac{A}{d} \frac{n e^2 \lambda v}{4 \alpha \theta} V$ ,

which leads at once to Ohm's law. Comparing with the equation  $i = \frac{A}{d} \sigma l$  where  $\sigma$  is the specific conductivity, we see that the

specific conductivity is given by  $\frac{n e^2 \lambda v}{4 \alpha \theta}$ , and is constant for a

given temperature. The only quantities in this expression which vary for different substances are  $\lambda$  and  $n$ . It does not seem probable that the variations in  $\lambda$  will be very great. The conductivity of a substance therefore should depend mainly upon  $n$ , the number of free electrons per unit volume. It is found experimentally that for most pure metals the conductivity is inversely proportional to the absolute temperature  $\theta$ . Since  $\alpha$  is a constant this leads to the result that  $n \lambda v$  is independent of the temperature.

#### 160. Relation of electrical and thermal conductivities.

**Law of Wiedemann and Franz.** Suppose that one part of a metallic conductor is heated. The electrons in the heated part have their velocities increased to correspond with the new value of the temperature. The electrons moving away from the heated part will therefore have a greater energy than those moving towards it. There will thus be a transference of energy from the hot to the cold part of the conductor, or in other words there will be conduction of heat through the metal by the electrons. It is known that non-conductors of electricity are very poor conductors of heat. It seems probable therefore that the conduction by the electrons is very much greater than that due to the atoms of the substance.

Assuming that the atmosphere of electrons in the metal can

be treated as a gas, the thermal conductivity  $k$  of the electrons should be given by

$$k = \frac{\pi}{8} n v \alpha \lambda \quad . \quad . \quad . \quad (133)$$

(see O. Meyer, *Kinetic Theory of Gases*), where  $n$ ,  $v$ ,  $\alpha$  and  $\lambda$  have the same significance as in the equation for electrical conductivity. Neglecting any conductivity due to the molecules this will be the thermal conductivity of the metal. Thus the ratio of the thermal to the electrical conductivity is given by

$$\frac{k}{\sigma} = \left( \frac{\pi}{8} n \alpha \lambda \right) / \left( \frac{n e^2 \lambda v}{4 \alpha \theta} \right) = \frac{\pi}{2} \left( \frac{\alpha}{e} \right)^2 \theta \quad (134)$$

The ratio of the thermal to the electrical conductivity should at a given temperature therefore be independent of the nature of the conductor. This is the well-known law of Wiedemann and Franz. Again this ratio should be directly proportional to the absolute temperature, that is, its temperature coefficient should be  $3.67 \times 10^{-3}$  per degree Centigrade. The following table shews that, for most pure metals, these deductions from the electron theory are very approximately true.

TABLE XV  
Ratio of thermal to electrical conductivity

Material	$k/\sigma$ at 18° C	Temperature coefficient
Copper	$6.7 \times 10^{10}$	$3.9 \times 10^{-3}$
Silver	$6.9 \times 10^{10}$	$3.7 \times 10^{-3}$
Gold	$7.1 \times 10^{10}$	$3.7 \times 10^{-3}$
Lead	$7.2 \times 10^{10}$	$4.0 \times 10^{-3}$
Tin	$7.4 \times 10^{10}$	$3.4 \times 10^{-3}$
Platinum	$7.5 \times 10^{10}$	$4.6 \times 10^{-3}$
Palladium	$7.5 \times 10^{10}$	$4.6 \times 10^{-3}$
Iron	$8.0 \times 10^{10}$	$4.3 \times 10^{-3}$

We can moreover obtain a numerical value for the expression (134). We have (131)

$$\alpha = \frac{1}{2} \frac{m v^2}{\theta} = \frac{1}{2} \frac{(9 \times 10^{-28}) (11 \times 10^6)^2}{273} = 2 \times 10^{-16} \text{ (approx.)},$$

substituting for  $m$  the mass of an electron (§ 51) and for  $v$  its thermal velocity at 0° C (273° abs.), while

$$e = 1.59 \times 10^{-20} \text{ e.m.u.}$$

$$\begin{aligned}\text{Hence} \quad \frac{h}{\sigma} &= \frac{\pi}{2} \left( \frac{2 \times 10^{-16}}{1.59 \times 10^{-20}} \right)^2 201 \\ &= 7.4 \times 10^{10}\end{aligned}$$

at a temperature of  $18^\circ \text{C}$ .

The agreement of the calculated value with the mean of the experimental results given in the table is very remarkable considering the nature of the assumptions made in the course of the argument, and the possible errors in the data used, and may be regarded as giving considerable weight to the electron theory of conduction.

Although the theory has proved so successful in this particular application it seems to be agreed generally that some further modification is required in our conception of the relation of the so-called free electrons to the atoms of the metal. Kamerlingh Onnes, has, for example, shewn that at certain temperatures appreciably above the absolute zero the resistance of certain metals suddenly falls to zero, or to a value so nearly zero that it is incapable of detection. For lead the critical temperature is  $2^\circ.45$  absolute, and somewhat lower for tin and mercury. This sudden fall of resistance is quite different to the gradual change of resistance with temperature, and the curve between resistance and temperature is discontinuous at the critical temperature.

The phenomena imply that at and below the critical temperature the electrons pass through the metal without communicating any of their energy to the fixed atoms. There is no corresponding change in the thermal conductivity, or indeed in any of the other physical properties of the metal. It has been suggested by Lundemann that the metal, at these low temperatures where the thermal agitations are sufficiently slight, forms a crystal structure in which the points on the space lattice are occupied alternately by atoms and electrons. A plane consisting only of electrons would be able to slip in any direction in its own plane without coming into collision with any atoms, and therefore without any appreciable loss of energy. The supraconductivity of these metals would thus be an extreme example of the property which renders them also ductile and malleable. At higher temperatures the excursions due to thermal agitation would be sufficiently large



to bring the electron, in some part of its path, into the plane occupied by atoms. Collisions would thus occur if the electron plane were moving parallel to its length, and resistance to the motion would thus arise. The whole subject is still under discussion and for a further account the student should consult the Report of the Solvay Conference published under the title *Atomes et Electrons*, 1923.

**161 Thermoelectric effects.** If we assume that the number of electrons per unit volume is different, in different conductors, we can obtain a qualitative explanation of the various thermoelectric effects. Thus, considering the electrons as a gas, if the number per unit volume in one conductor is greater than in the other, the electronic pressure in the first will be greater than that in the second; so that when the two are brought into metallic contact there will be a flow of electrons from the first to the second, until the charges carried by the electrons so transferred produce a difference of potential sufficient to prevent any further transference. There will thus be established a permanent contact difference of potential between the two metals.

Again if we wish to transfer electrons from the metal of lower to the metal of higher electronic pressure work must be done against this difference of pressure. Thus when a current is sent through the junction work must be done and energy is absorbed in the form of heat. Similarly if the current is reversed energy is liberated in the form of heat. This is obviously the Peltier effect.

An expression can easily be obtained for this effect. Let  $\pi$  be the work done per unit quantity of electricity.  $\pi$  is the coefficient of the Peltier effect. Thus

$$\pi = \int_{v_1}^{v_2} p dv.$$

Now by the kinetic theory of gases

$$p = \frac{1}{3}nmv^2 = \frac{2}{3}na\theta$$

and since unit quantity of electricity contains  $\frac{1}{e}$  electrons

(where  $e$  is the electronic charge) the volume  $v$  occupied by the  $\frac{1}{e}$  electrons in the unit quantity transferred will be  $\frac{1}{ne}$  where  $n$  is the number of electrons per unit volume

$$\therefore n = \frac{1}{ev} \quad \text{and} \quad p = \frac{2}{3} \frac{\alpha \theta}{ev},$$

$$\begin{aligned} \therefore \pi &= \int_{v_1}^{v_2} p dv = \frac{2}{3} \frac{\alpha}{e} \theta \int_{v_1}^{v_2} \frac{dv}{v} \\ &= \frac{2}{3} \frac{\alpha}{e} \theta \log_e \frac{v_2}{v_1} \\ &= \frac{2}{3} \frac{\alpha}{e} \theta \log_e \frac{N_1}{N_2}, \end{aligned}$$

where  $N_1$  and  $N_2$  are the numbers of electrons per unit volume in the two conductors. This result was given by Sir J J Thomson

The phenomena just described have been dealt with to illustrate the nature of the electron theory of matter and the kind of progress which has already been made. In many directions, however, the theory is as yet only tentative, and the underlying assumptions still under discussion. In particular until the actual arrangement of electrons in the atomic systems is more accurately determined, and until more is known as to the nature of the action which causes energy to be radiated and absorbed in definite "quanta," the principles of the subject cannot be said to have been finally settled. For this reason, as well as for the reason that the mathematical analysis involved is often of the most intricate kind, we shall not pursue the subject further in the present volume.

## REFERENCES

### GENERAL

The subject matter of this chapter is a very wide one and it has been impossible to enter into the minute details. The following books may be consulted for further particulars.

A SOMMERFELD *Atombau und Spektrallinien* (3rd Ed.) (English translation, 1924)

N R CAMPBELL *The Structure of the Atom*, 1923.

— *Series Spectra*, 1923

- N BOHR *The Theory of Spectra and Atomic Construction* 1923  
 — *On the Application of the Quantum Theory to Atomic Structure*, Part I,  
 1924 Part II (to appear shortly) (Published by the Cambridge  
 Philosophical Society)  
*Atomes et Electrons* Report of the Solvay Conference, 1923.  
 Sir J. J. THOMSON *Franklin Lectures* 1923

For a more popular account of the various theories of atomic structure  
 see also

ANDRADE *The Structure of the Atom* 1923.

Owing to the rapid growth of the subject and the constant succession of  
 modifications of and additions to the theories, the student can hardly be  
 recommended to consult the original papers. Full references will be found  
 in the books by Sommerfeld and Campbell

For the older electron theories of the atom see

J. J. THOMSON, *Cathode Ray Theory of Matter* 1907

TABLE XVI

Table of Atomic Data

Electronic charge, $e$	$1.771 \times 10^{-10}$ e.s. units
	$1.59 \times 10^{-20}$ e.m. units
$e/m$ for electron	$1.774 \times 10^9$ e.m. units per gm
Mass of an electron	$8.96 \times 10^{-28}$ gm.
Radius of electron	$1.9 \times 10^{-11}$ cm
$h$ (quantum constant)	$6.55 \times 10^{-27}$ erg sec
$E/m$ for $\alpha$ -particle	$4.823 \times 10^8$ e.m. units per gm
Mass of a particle (helium atom)	$6.5 \times 10^{-24}$ gm
$e/m$ , hydrogen ion in solution	$9.649 \times 10^7$ e.m. units per gm
Mass of hydrogen atom	$1.66 \times 10^{-24}$ gm
Radius of hydrogen molecule	$1.21 \times 10^{-8}$ cm
Gas molecules per c.c. at N.T.P.	$2.705 \times 10^{19}$
Number of molecules in 1 gm mol	$6.16 \times 10^{23}$
Radius of nucleus of hydro- gen atom	$< 10^{-13}$ cm
Radius of nucleus of platinum atom	$10^{-12}$ cm approx.
Radius of inner ring of elec- trons ( $K$ ring) for platinum atom	$10^{-10}$ cm.
Wave length of X-rays (char- acteristic $K$ rays from silver)	$0.56 \times 10^{-8}$ cm
Wave length of $\gamma$ rays	$10^{-9} - 10^{-10}$ cm

# INDEX

*References are to pages*

- $\alpha$  particle, charge on, 203
  - collision of, with hydrogen atom, 216, light atoms, 219, heavy atoms, 218
  - dimensions of, 220
  - disintegration of atoms by, 220
  - nature of, 203
  - number of, emitted by radium, 205
  - range of, 207, 284
  - track of, 41
- $\alpha$  rays, absorption of, 206, 209
  - heating effect of, 281
  - ionization by, 209
  - loss of velocity of, 208
  - scattering of, 214, 217
- see also  $\alpha$ -particle*
- Absorption of  $\alpha$  rays, 206, 209
  - of  $\beta$ -rays, 229, 231
  - of  $\gamma$ -rays, 234
  - of  $\lambda$  rays, 183 *et seq*
- Actinium, origin of, 275
  - radio activity of, 272
- Active deposit from emanation, 261, analysis of, 265
- Adiabatic invariance, principle of, 315
- Aston, 111
- Atom, constitution of, 287 *et seq*
  - disintegration of, by  $\alpha$  particles, 220, radio-active, 243 *et seq*
  - orientation of, 311
  - theory of, Langmuir, 308, Rutherford-Bohr, 295 Thomson, 292
- Atomic energy, liberation of, 220
- Atomic disintegration, 220, 243 *et seq*
- Atomic levels, 192, 306 *et seq*
- Atomic nuclei, structure of, 289
- Atomic number, 164
- Average life of radio active atom, 251
- Avogadro's number, 46, 50, 51
- Azimuthal quantum number, 302
- $\beta$  rays, absorption of, 229
  - change of velocity of, during absorption, 231
  - characteristic, 240
  - determination of  $e/m$  for, 223, 227
  - heating effect of, 281
  - magnetic deflection of, 222
  - nature of, 222
  - production of  $\gamma$  rays from, 237
  - production of, from  $\gamma$  rays, 237, 240
  - scattering of, 231
  - variation of mass with velocity for, 227
- Balmer's series for hydrogen, theory of, 298
- Barlin, 162, 187, 188
- Becquerel, 222
- Bielei, 220
- Bohr, 193, 296, 303, 309
- Bragg, Sir W. H., 160, 209
- Bragg, W. L., 160, 177
- Brownian movement, 46
- Brush discharge, 72
- Bucherer, 228
- Campbell, N. R., 283
- Curie, 69
- Cathode fall of potential, 8f glow, 75
- Cathode rays, 86 *et seq*
  - determination of  $e/m$  for, 95, 98
  - magnetic spectrum of, 98
  - nature of, 86
  - production of X-rays from, 154, 156, 178, 181, 189
  - velocity of, 95, 100
- see also electron*
- Chadwick, 218, 220
- Chamber, ionization, 14
- Characteristic  $\beta$  rays, 240
- Characteristic  $\gamma$  rays, 234, 241
- Characteristic X-radiation, 180 *et seq*
  - application of quantum relations to, 191
  - conditions for excitation of, 189
  - fine structure of, 310
  - Moseley's relation for, 182
  - secondary, 186
  - theory of, 192, 309
  - wave lengths of, 182, 195
- Condensation experiments, apparatus for, 38, 41
  - measurement of  $e$  by, 41
  - tracks of particles by, 41
- Condensation on charged particles, 36
- Conductivity, of discharge tube, 80
  - of flames, 130
  - of gases, 7, *see also* gaseous conduction
  - of metals, 316
  - of salt vapours, 134
- Coolidge tube, 153
- Corpuscular radiation, secondary, 194
- Crookes, Sir W., 1, 86, 243
- Crookes dark space, 76, 83
  - field in, 79
  - ionization in, 80

- Crookes*, 161, 183, 230  
*Curie*, 223, 256, 260, 284  
 Curie (unit), 261, 262  
 Current, ionization, measurement of,  
   10, 13  
   saturation, 16  
   variation of, with pressure, 17; with  
   potential, 15
- $\delta$ -rays, 263
- Dark discharge, 73
- Dark space, Crookes, 76, 79  
   Faraday, 76, 79
- de Broglie*, 197
- Deuss*, 284
- Discharge, at low pressure, 75  
   brush, 73  
   dark, 73  
   field in, 77  
   number of ions in parts of, 70  
   spark, 67 *et seq*  
   theory of, 82
- Discharge tube, 75 *et seq*
- Disintegration of atoms by collision,  
   220  
   of uranium, 243  
   theory of radio activity, 246, 248  
   *et seq*
- Dolezalek electrometer, 11
- Dosage, X-ray, 200
- Duane*, 282
- e*, collected values of, 51  
   determination of, 41, by Brownian  
   movement, 46, by condensation  
   experiments, 42, Millikan's ex-  
   periments, 43
- e/m*, for  $\alpha$ -rays, 202  
   for  $\beta$ -rays, 223, 227  
   for cathode rays, 95, 98  
   for the muons, 119  
   table of values of, 99  
   variation of, with velocity, 227
- Electric field, action of, on charged  
   particles, 92  
   in discharge tube, 77  
   in flame, 132  
   in X ray pulse, 158  
   motion of ions in an, 19
- Electromagnetic mass, 225  
   variation of, with velocity, 227
- Electrometer, Dolezalek, 11  
   measurement of current by, 10, 13
- Electron, 3  
   as negative carrier in gaseous con-  
   duction, 31, 32  
   atomic nature of, 45  
   charge on, see *e*  
   mass of, 225, 227  
   radiation from, 156
- Electron (*cont*)  
   radius of, 227  
   velocity of thermal agitation of, 317  
   see also  $\beta$  rays, photo electrons,  
   thermuons
- Electron theory of atom, 287 *et seq*  
   of metallic conduction, 310  
   of thermoelectricity, 321  
   of valency, 305
- Electrons, arrangement of, in atom,  
   292, 295, 303  
   number of, in atom, 161, 233, 289
- Electroscope, measurement of current  
   by, 10, 13  
   simple, 7, 237  
   Wilson, 12
- Elliptic orbits, 301
- Ellis*, 239, 240, 242
- Excited activity, 262
- Expansion apparatus, 38, 41
- Faraday cylinder, 88  
   dark space, 76, 83, field in, 79,  
   ionization in, 80  
   tubes, 156
- Flames, conducting power of gases  
   from, 8  
   conductivity of, 130  
   distribution of electric field in,  
   131  
   relation between current and poten-  
   tial in, 134
- Fluorescent X-radiation, see charac-  
   teristic X-radiation
- Friedrich and Knipping*, 166
- $\gamma$  rays, absorption of, 234  
   characteristic, 234  
   nature of, 233  
   production of, 237, 241  
   production of  $\beta$ -rays from, 237  
   secondary, 237  
   wave length of, 235
- Gaseous conduction, measurement of,  
   10  
   relation between current and poten-  
   tial for, 16, 20  
   theory of, 9, 17
- Geiger*, 215, 284
- Geological age, 279
- Glow, cathode, 75 *et seq*  
   negative, 75 *et seq*
- Haga and Windt*, 165
- Half value period, 251
- Helium, production of, from uranium,  
   279, from  $\alpha$ -particles, 203  
   spectrum of ionized, 299
- Helium nucleus, dimensions of, 219  
   structure of, 290

- Homogeneous X radiation, *see* characteristic X-radiation
- Hull, 180
- Hydrogen atom, electrochemical equivalent of, 46  
mass of, 51  
structure of, 300
- Hydrogen, effect of, on thermionic emission, 124  
ionization potential of, 63, 701  
production of, from atomic nuclei, 220
- Hydrogen spectrum, theory of, 296
- Interference of X-rays, 165 *et seq*
- Inverse square law, verification of, for atomic encounters, 218  
failure of, for close encounters, 219
- Ionic mobilities, *see* mobility of ions
- Ionium, 279
- Ionization by collision, 51 *et seq*, for negative ions, 54, for positive ions, 65  
chamber, 14  
current, *see* current, ionization potentials, 63, 301  
produced by  $\alpha$ -rays, 209, by ultra-violet light, 138, by X-rays, 199  
theory of gaseous conduction, 9, 17
- Ions, charge on, *see*  $e$   
doubly charged, 46  
motion of, under electric field, 19  
mobilities of, 19, 23, 24  
nature of gaseous, 30  
number of, produced by  $\alpha$  rays, 281;  
by  $\beta$  rays, 281, by collision, 61,  
by X-rays, 199, 200  
recombination of, 18, 12
- Isotopes, 114  
radio-active, 276  
theory of, 290
- J radiation, 183
- K discontinuity, 185, 193, 195  
orbits, 305  
radiation, 181, 182, 195, 310
- Kanalstrahlen, *see* positive rays
- Kapitza, 208
- Kaufmann, 98, 223
- L discontinuity, 185, 186, 194, 195  
orbits, 305  
radiation, 181, 182, 195, 310
- Langmuir, 24, 33
- Langmuir, 127, 301, 309
- Larmor, 315
- Lane, 165, 166
- Lead from radio-active substances, 280
- Lindemann, 320
- Loeb, 32
- Loewy, 228, 313
- Lyman series for hydrogen, 299
- Magnetic field, action of, on charged particle, 90  
decomposition of spectral lines by, 312  
orientation of atoms in, 311
- Marsden, 216
- Mass, electromagnetic, 225, variation of, with velocity, 282  
of electron, 100  
of hydrogen atom, 51
- Mass-spectrograph, 111
- Maxwell-Boltzmann law for thermions, 123
- McClellan, 286
- Metallic conduction, theory of, 316
- Milne, 261
- Mittelman, 13, 141
- Mobility of ions, 19  
calculation of, 28  
effect of pressure on, 30  
in different gases, 27  
measurement of, 23, 24
- Negative parabolas, 109
- Nitrogen atom, disintegration of, 220
- Non polar compounds, 308
- Nuclear charge, 219  
levels, 241  
theory of atom, 295 *et seq*
- Nucleus, dimensions of, 289  
disintegration of, 220  
structure of, 289
- Ohm's law, 318
- Ordinary materials, radio activity of, 285
- Paschen's law, 70
- Periodic classification of elements, 294, 305
- Perrin, 46, 87
- Phosphorescence, 151
- Photo-electric effect, 147 *et seq*  
critical wave length to excite, 138  
effect of polarization on, 148  
in gases, 138  
in non-metals, 150  
magnitude of, 145
- Photo electric fatigue, 150
- Photo electrons, 137 *et seq*  
distribution of velocities among, 145  
 $e/m$  for, 138  
maximum velocity of, and wave length, 140
- Pickering-Fowler series, 300

- Planck's constant, 142  
law, 142, *see also* quantum theory
- Polar compounds, 308
- Polonium, 271
- Positive column, 76  
electric field in, 79  
ionization in, 80
- Positive electron, 289  
thermionic emission, 118, 126
- Positive ray analysis, 110  
parabolas, 103
- Positive rays, 101  
electrical measurement of, 114  
measurement of  $E/m$  for, 102  
nature of, 101, 108
- Potassium, radio-activity of, 286
- Pressure, effect of, on ionic mobilities, 30  
on saturation current, 17
- Proton, 289
- Quantum number, 296  
azimuthal, 302  
radial, 302  
"third," 311
- Quantum theory, 142 *et seq.*, 180, 189,  
192, 198, 230, 241  
of atomic structure, 296  
of Zeeman effect, 315
- Radial quantum number, 302
- Radiant matter, 2
- Radio-active constant, 245  
change, theory of, 246, 248  
elements, table of, 274, position of,  
in Periodic table, 275, 277  
equilibrium, 251, 278  
transformations, theory of, 248
- Radio-activity of ordinary matter, 285  
of manum, 243  
theory of, 248
- Radium, heating effect of, 281  
nature of, 256 *et seq.*  
origin of, 278
- Radium A, 266
- Radium B, 267  
separation of, 268
- Radium C, 267  
complex disintegration of, 269  
emission of charge by, 266
- Radium D, 271
- Radium E, 271
- Radium emanation, 257 *et seq.*  
active deposit from, 262  
boiling point of, 259  
density of, 258  
rate of decay of, 259  
rate of escape of, 261
- Ramsay and Gray*, 258
- Range of  $\alpha$ -particle, 207 *et seq.*  
and rate of decay, 284
- Recoil atoms, 264
- Recombination, coefficient of, 18  
measurement of, 32, 33
- Regener*, 204
- Resonance potentials, 63, 143
- Richardson, O. W.*, 117, 123
- Richardson's law of thermionic emission, 119, 122
- Robinson*, 197
- Röntgen*, 153
- Runge and Paschen*, 311
- Rutherford, Sir E.*, 23, 32, 204, 218,  
219, 235, 238, 241, 249, 257, 261,  
286, 289, 292
- Rydberg's constant**, 299
- Saturation current, 16, 17
- Scattered X-radiation, 160  
distribution of, 161  
energy of, 163  
polarization of, 161
- Scattering of  $\alpha$ -rays, 214  
of  $\beta$  rays, 231  
of  $\gamma$ -rays, 237
- Secondary  $\beta$ -radiation, 240  
corpuscular radiation, 194, 197  
 $\gamma$ -radiation, 237 *et seq.*  
X radiation, 160, 186
- Siegbahn*, 195
- Soddy*, 276
- Sommerfeld*, 303, 310
- Space lattice, 167
- Spark discharge, theory of, 67
- Sparkling potentials, 69  
Paschen's law of, 70  
variation with temperature, 71
- Specific conductivity, 318
- Spectrum,  $\beta$ -ray, 240  
hydrogen, theory of, 296  
X-ray, 178 *et seq.*, 309
- Stark effect, 316
- Stationary orbits, 296, 298 *et seq.*
- Stokes, Sir G. G.*, 156
- Stokes' law, 42, 45, 49
- Stopping power for  $\alpha$  rays, 213
- Strutt*, 279
- Supraconductivity, 320
- Suspensions, distribution of particles  
in, 48
- Sylvia, structure of, 177
- Thermal conductivity, 318
- Thermionic emission, 117 *et seq.*  
effect of hydrogen on, 124  
from different substances, 125  
measurement of, 118  
of positive electricity, 126  
variation of, with temperature, 119

- Thermionic valve, 127  
 Thermons, 117  
   distribution of velocities among, 123  
   *c/m* for, 119  
   nature of, 118  
 Thermoelectricity, theory of, 321  
 "Third" quantum number, 311  
 Thomson, Sir J. J., 21, 41, 78, 89, 93, 102, 134, 157, 163, 291, 293, 295, 301, 308, 322  
 Thorium, disintegration of, 272  
  
 Wave length, critical, 138, 191  
   of  $\gamma$ -rays, 235  
   of X rays, 175, 195  
 Webster, 191  
 Wehnelt cathode, 125  
 Whiddington, 189  
 Wiedemann and Franz, law of, 318  
 Wilson, C. T. R., 7, 36, 37, 41  
 Wilson, H. A., 135  
  
 X-rays, 153 *et seq*  
   absorption of, 183, coefficient of, 184, discontinuities in, 185  
   characteristic, 180, *see also* characteristic X-radiation  
   classical theory of, 186  
   continuous spectrum of, 178  
   corporeal radiation produced by, 184  
   determination of wave length of, 173  
   interference of, 165  
   ionization by, 199  
   origin of, 154  
   polarization of, 161  
   reflection of, 169  
   scattering of, 160  
   track of beam of, 41  
 X ray dosage, 200  
   spectra, theory of, 192, 309  
   spectrometer, 173  
  
 Zeeman effect, 312